# Chem Ed

## EDITORIALLY SPEAKING

Nonmilitary Defense—Chemical and Biological Defenses in Perspective," number 26 of the Advances in Chemistry Series published by the American Chemical Society, is the most comprehensive single-volume source of information on this subject that has been made available to the public. It is the transcript of the symposium with this title held at the Cleveland ACS meeting in April, 1960. Chemists in the classroom, who are training future citizens, should read this book.

It is frank and informative. It pulls no punches. It is designed to fight apathy, not by alarming the reader but by informing him. Its target is the scientist and through him the otherwise well-informed layman. Again and again throughout the papers, contributed by the foremost authorities in the country, the theme recurs: CW and BW are threats, not one whit diminished by being overshadowed in the public mind by the threat of nuclear weapons and radiological hazards. Furthermore, the informed scientist-citizen, at the same time that he recoils in horror at the thought of a war fought with chemical and biological weapons, owes it to himself and his fellow citizens who look to him for guidance to know the facts. These facts, directly stated and honestly appraised in this volume, include: what "weapons" exist, what their effects are, what protections and treatments are known, and how much research still is needed before plans for the safety of our population can be considered satisfactory.

The chemistry classroom is not the place for elaborate sermons on moral issues. At the same time it is not a place where they should be elaborately ignored. No one can claim the adjective "humane" for any weapon. Only the ignorant can claim that a chemistry professor who mentions the crying need for more research on the mode of action of nerve gases is urging his students to abandon moral principles. These materials *do* exist, our potential enemies *do* have them, the protection of virtually our entire population *is* an urgent concern. What could be more morally right and humane than to help supply the scientific knowledge, in its appropriate context, that can save life? As one speaker so aptly stated, "The research in question is concerned with basic problems of the central object of all scientific endeavor, namely man." Moreover, the same is true of all moral issues. Man's use of his knowledge is the problem, never his gaining of that knowledge.

The chemistry professor will find many bits of information in this book which can serve as the illustration of a principle which the student will remember and ponder. For example: Sanitary engineering procedures can insure essentially sterile water for a community, but no procedures exist for delivering sterile air. When the particle size of a disease-bearing aerosol is 1.0 micron, the infecting dose will be only one-seventeenth as much as that required with particles of 12.0 microns in diameter. Nerve gases act by inhibiting the enzyme cholinesterase from acting on the acetylcholine formed when muscles contract; when this "remover of the ashes does not operate, the fire goes out." Pathogenic organisms can be identified rapidly by an ingenious technique taking advantage of the action by specific antibodies tagged with fluorescent dye. If microscopic examination with ultraviolet light reveals fluorescence of the organism, its identity is then known. Nerve gases are organic esters of substituted phosphoric acids (structural formulas given)—the Russians captured a German factory for producing these, dismantled it and reconstructed it in Russia. Eighty-five per cent of the Russian population has completed a ten hour course in anti-air defense including BW and CW protection and decontamination.

"Taboo" is a word with uncomfortable semantics for the educated person. Yet it is a most appropriate term for the attitude of many toward this whole subject. Like all ignorance, taboos cannot breathe the fresh air of information. Chemistry classrooms ought to have good ventilation.

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# Hydrocarbons in Petroleum

Petroleum, one of the most important natural resources in our world today, is a very interesting and intriguing chemical substance. Although it contains small amounts of compounds of sulfur, of nitrogen, of oxygen, and of metallic constituents, petroleum is largely hydrocarbon material, with molecules ranging in size from 1 to 50 or more carbon atoms and comprising a diversity of molecular types. Because petroleum contains many hydrocarbon compounds which are of themselves important chemicals of commerce, and because chemicals derived from petroleum are increasing greatly in number and importance, petroleum has come to be called nature's storehouse of chemicals.

Going back into history, we find that early man long wondered about the thick dark liquid that oozed from the earth or floated on natural waters. He learned many centuries ago that this strange substance would burn and give out great heat and light. Petroleum, or some portion of it, as bitumen or asphalt, is mentioned in the Bible, and records show that asphalt was used by man as early as 3800 B.C. (*1*, *2*). Petroleum was found as an oily liquid exuding from the surface of the earth in tar springs or on shores of lakes or rising from springs beneath the beds of rivers in many places on earth, as Rumania, Iran, Italy, Trinidad, Cuba, India, and later the United States. Surface wells were dug to increase the quantity available.

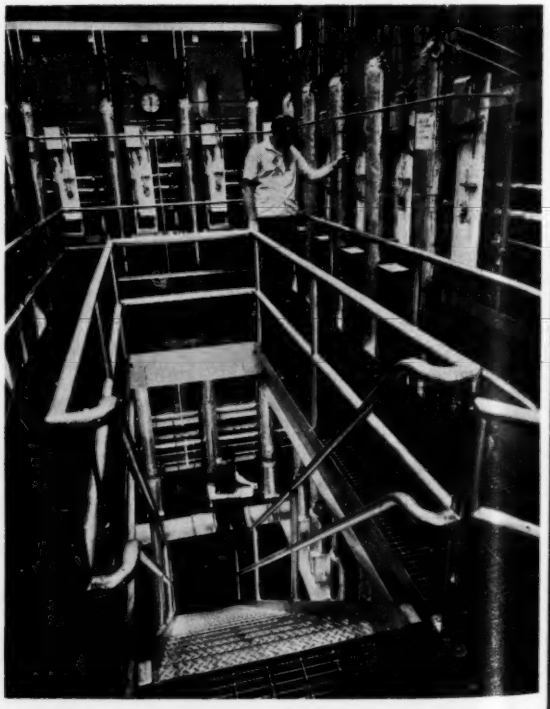
But it remained for the first drilled petroleum well to start the great flow of crude oil from the earth—the famous Drake well, located near Titusville, Pennsylvania, completed in 1859 to a depth of $69\frac{1}{2}$ ft, with a production of about 25 barrels per day. Since then, the annual production of petroleum from the continental United States has grown to truly astonishing amounts, as follows, in billions of barrels per year: 0.000002 in 1860; 0.026 in 1880; 0.064 in 1900; 0.44 in 1920; 1.3 in 1940; nearly 2.0 in 1950; and nearly 3.5 in 1960. The "proved" reserves of petroleum in the continental United States have also increased greatly, as follows in billions of barrels: 3 in 1900; 7 in 1920; 19 in 1940; and 35 in 1960. The ratio of the proved reserves to the annual production in any given year has decreased somewhat over the years: 21/1 in 1910; 16/1 in 1920; 15/1 in 1930; 15/1 in 1940; 13/1 in 1950; and about 10/1 in 1960.

## Early Work

In 1906, Coates (*3*), one of the early investigators of the composition of petroleum, stated: "It is exceedingly difficult to get the hydrocarbons (from petroleum) in a state of purity. Indeed, I do not think it can be done by distillation." In 1924, Anderson and Erskine (*4*) published the results of their work on the composition of "natural" gasoline. In 1926, Brown and Carr (*5*) published the results of the first investigation in which appreciable quantities of "pure" hydrocarbons were separated from petroleum by systematic distillation. From 1932 to 1938, notable contributions on the composition of petroleum were published by Fenske and co-workers (*6–10*). The state of the existing knowledge in 1928 was well summarized by Gruse (*11*).

A summary of other work on the composition of petroleum, including hydrocarbon constituents, sulfur compounds, nitrogen compounds, oxygen compounds, and metallic constituents is given by Rossini, Mair, and Streiff (*13*), Lochte (*14*), Gruse and Stevens (*15*), and Smith, Dunning, Rall, and Ball (*16*).

## —The cover—



The whole story of the API distillation laboratory is better revealed by this photograph. The 14 distilling assemblies, each with a separating power of 200 theoretical plates, extend through two floors. The laboratory operates 24 hours per day, seven days per week.

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## The API Research Project 6

In 1927, the American Petroleum Institute Research Project 6 was established at the National Bureau of Standards under the direction of Edward W. Washburn to investigate the hydrocarbon constituents of petroleum. Washburn continued to direct the work until his untimely death early in 1934. The writer then became Director of the Project and has continued actively in it for 26 years. For the past ten years, Beveridge J. Mair has been Associate Director, becoming Director in July, 1960.

An interesting historical account of the API Research Project 6 has been prepared by Hill (*12*). A complete list of the many professional investigators who have been associated with the Project from 1927 to 1952 is given in reference *13*. The purpose of the present report is to give a self-consistent story of hydrocarbons in petroleum as developed by the approximately 500 man-years of work put on this problem by the API Research Project 6.

To get at the heart of the composition of petroleum, and to lay open the components in a way that accurately discloses their identity, the API Research Project 6 has had one representative petroleum continually under exhaustive fractionation since 1928. The work of the Project has established that substantially all of the hydrocarbons in petroleum are composed of only three kinds of component parts, namely, paraffin groups, cycloparaffin (or naphthalene) groups, and aromatic groups. Examples of these three classes of component parts are shown in Figure 1.

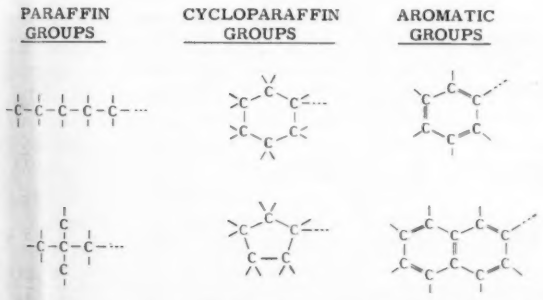


Figure 1. The three types of hydrocarbon groups from which substantially all the hydrocarbons in petroleum are made.

There are three broad classes of hydrocarbons in petroleum, as follows: (1) paraffins, which are those molecules containing only paraffin groups; (2) cycloparaffins, which are those molecules containing one or more cycloparaffin groups with or without paraffin groups; and (3) aromatics, which are those molecules containing one or more aromatic groups, with or without cycloparaffin groups and/or paraffin groups.

The precise manner in which the above groups are combined to form the individual compounds can be originally determined with accuracy only by the actual isolation of the individual compounds. Fortunately, this exhaustive fractionation need be done only once. When this basic information becomes known, shortcut methods can be used to make rapid analyses of the compounds previously established to be components of petroleum.

One of the important aims of the work has been to increase our knowledge of the composition of different petroleums the world over. Some years ago, the Project completed an extended investigation on the composition of the gasoline fraction of petroleum from seven fields in the continental United States, each representing major production. The results of this investigation, supported by related findings on petroleum from other lands, provide a framework which makes it possible to translate to any new petroleum the basic information and data obtained on the one representative petroleum of the API Research Project 6.

In addition to the foregoing information, one of the important products of the work has been the development of fractionating processes of high separating power.

## General Plan of Operation

The general plan of operation on the one representative petroleum has been substantially as follows: (1) one representative petroleum, more or less "intermediate" in character, was selected for examination, from the Brett No. 6 well in the Ponca City field in Oklahoma; (2) a sufficient quantity (approximately 500 gal.) of this representative petroleum was taken as starting material, so that after appropriate fractionation the principal components would be expected to be present in an adequate amount to permit identification; (3) the fractionation of the material was (and is) carried out in such a way as to neither destroy constituents already present nor to produce new ones previously absent; (4) the entire petroleum is separated by distillation (at pressures low enough to keep the distilling temperature below 200°C) into convenient broad fractions, as the "gas," "gasoline," "kerosine," "light gas oil," "heavy gas oil and light lubricating distillate," and "lubricant" fractions; (5) the "gas" fraction was separated by distillation alone; (6) each of the remaining broad fractions was (or is being) separated, by the use of the proper combination of fractionating processes, into classes and subclasses of hydrocarbons including, as appropriate, normal paraffins, branched paraffins, mono-cycloparaffins, bicycloparaffins, higher cycloparaffins, mononuclear aromatics, dinuclear aromatics, and higher nuclear aromatics; (7) each subclass of hydrocarbons is separated by distillation with high separating power according to boiling point or molecular size to produce "homogeneous" fractions containing molecules of substantially the same size and class; (8) the homogeneous fractions are further fractionated in so far as possible to yield the principal individual compounds; (9) each of the homogeneous fractions which remains unresolved with respect to individual compounds is examined as to physical and spectrographic properties in order to derive as much information as possible concerning the composition of the unresolved homogeneous fraction.

We have learned that the more thoroughly we examine the lower boiling broad fractions, as the gas, gasoline, and kerosine fractions, the more we can learn from given observations on the higher boiling fractions.

### Fractionating Processes Used

The method which has been developed by the Project for separating petroleum into its principal constituents may be described as the systematic interlocking of the basic processes of fractionation and their variations. The order in which the various fractionating processes are used to separate a given fraction of petroleum into its main constituents is determined by the effectiveness of each given process in furthering the separation already attained by the preceding process. The fractionating processes used by the Project have included five forms of distillation, two forms of extraction, four forms of adsorption, two forms of crystallization, and two forms of separation with solid molecular or clathrate compounds:

*Distillation* (liquid and gas phases): (*a*) regular, at one pressure (30, 55, 214, or 760 mm Hg); (*b*) alternately at different pressures (30, 55, 214, and 760 mm Hg); (*c*) at very low pressures (0.01 to 0.1 mm Hg); (*d*) azeotropically, with regular polar organic compounds; (*e*) azeotropically, with fluoro-organic compounds.

*Extraction* (two liquid phases): (*a*) with one solvent phase; (*b*) with two solvent phases.

*Adsorption* (liquid or gas phase and solid-adsorbed phase): (*a*) regular; (*b*) with one or more added components.

*Crystallization* (liquid and solid phases): (*a*) regular; (*b*) with a selected solvent.

*Formation of molecular or clathrate compounds:* (*a*) in batch process; (*b*) in column with "reflux."

For details of the fractionating processes used in this work, the reader may consult references *13* and *17–20*.

### Summary of the Present Status of the Work

Using the fractionating processes mentioned above, and operating systematically and exhaustively according to plan, the Project has isolated 175 hydrocarbon compounds from its one representative petroleum as of June 30, 1960. A description of the source and character of this representative petroleum is given in reference *13*. Additional details may be found in reference *22*.

Table 1 gives a summary of the amounts of the broad fractions constituted by the hydrocarbons isolated from this representative petroleum. Table 2 gives the distribution, by class and broad fraction, of the hydrocarbons isolated. Table 3 gives the distribution (by class and number of carbon atoms per molecule) of the hydrocarbons isolated, except for the normal paraffins, of which all 32 members (from methane, $CH_4$, to normal tritriacontane, $C_{33}H_{68}$, inclusive) have been isolated.

Table 4 lists the 175 hydrocarbons isolated, according to class, and gives the normal boiling point and the amount of the given compound in this petroleum.

**Table 1. Summary of the Amounts of the Broad Fractions Constituted by the Hydrocarbons Isolated from the Representative Petroleum**

| Broad fraction | Gas | Gasoline | Kerosine | Light gas oil | Heavy gas oil and light lubricating distillate | Lubricant fraction | Residue | Total |
|---|---|---|---|---|---|---|---|---|
| Boiling range at 1 atm. (°C) | <40° | 40°–180° | 180°–230° | 230°–305° | 305°–405° | 405°–515° | ... | ... |
| Range of normal paraffins | $C_1$–$C_5$ | $C_6$–$C_{10}$ | $C_{11}$ and $C_{12}$ | $C_{13}$–$C_{17}$ | $C_{18}$–$C_{25}$ | $C_{26}$–$C_{38}$ | ... | ... |
| Estimated percentage of the original petroleum constituted by the given fraction | 4 | 33.2 | 12.7 | 18.6 | 14.5 | 10.0 | 7 | 100 |
| Number of compounds isolated | 7 | 101 | 37 | 12 | 10 | 8 | ... | 175 |
| Estimated percentage of the fraction accounted for by the hydrocarbons isolated | 100 | 82.3 | 38.4 | 30.2 | 20.5 | 9.9 | ... | ... |
| Estimated percentage of the original petroleum accounted for by the hydrocarbons isolated | 4.0 | $27.3_3$ | $4.8_4$ | $5.6_1$ | $2.9_7$ | $0.9_9$ | ... | $45.7_4$ |

**Table 2. Distribution, by Class and Broad Fraction, of the Hydrocarbons Isolated from the Representative Petroleum**

| Broad fraction | Gas | Gasoline | Kerosine | Light gas oil | Heavy gas oil and light lubricating distillate | Lubricant fraction | Total |
|---|---|---|---|---|---|---|---|
| Boiling range at 1 atm. (°C) | <40° | 40°–180° | 180°–230° | 230°–305° | 305°–405° | 405°–515° | ... |
| Range of normal paraffins | $C_1$–$C_5$ | $C_6$–$C_{10}$ | $C_{11}$–$C_{12}$ | $C_{13}$–$C_{17}$ | $C_{18}$–$C_{25}$ | $C_{26}$–$C_{38}$ | ... |
| | | | *Number of Compounds* | | | | |
| Classes of hydrocarbons | | | | | | | |
| Normal paraffins | 5 | 5 | 2 | 5 | 8 | 8 | 33 |
| Branched paraffins | 2 | 35 | ... | ... | ... | ... | 37 |
| Alkyl cyclopentanes | ... | 22 | ... | ... | ... | ... | 22 |
| Alkyl cyclohexanes | ... | 13 | 1 | ... | ... | ... | 14 |
| Alkyl cycloheptanes | ... | 1 | ... | ... | ... | ... | 1 |
| Bicycloparaffins | ... | 4 | 6 | ... | ... | ... | 10 |
| Tricycloparaffins | ... | ... | 1 | ... | ... | ... | 1 |
| Alkyl benzenes | ... | 20 | 20 | ... | ... | ... | 40 |
| Aromatic cycloparaffins | ... | 1 | 6 | 1 | ... | ... | 8 |
| Dinuclear aromatics | ... | ... | 1 | 6 | 1 | ... | 8 |
| Trinuclear aromatics | ... | ... | ... | ... | 1 | ... | 1 |
| Total | 7 | 101 | 37 | 12 | 10 | 8 | 175 |

### Fractions by Distillation

*Gas.* The gas fraction, taken as the material normally boiling up to 40°C, has been fully accounted for in terms of all the possible normal paraffins and branched paraffins, $C_1$ to $C_5$, except for 2,2-dimethyl propane which is believed to be present only in extremely small or trace amounts. These compounds are listed in Table 4.

*Gasoline.* The hydrocarbons of this fraction, taken as the material normally boiling from 40° to 180°C, consist of normal ($C_6$ to $C_{10}$) and branched paraffins, mono- and bicycloparaffins, and mononuclear aromatics. In Table 4 are listed the compounds isolated, together with those compounds normally boiling up to 132°C which are believed to be present in extremely small amounts.

All of the five possible normal paraffins, $C_6$ to $C_{10}$, have been accounted for. All of the possible branched paraffins in the range 40° to 132°C have been isolated, except for six compounds which are believed to be present only in extremely small amounts. Also isolated were eight branched paraffins in the range 132° to 180°C. The monocycloparaffins in the gasoline fraction consist of alkyl cyclopentanes, alkyl cyclohexanes, and very small amounts of alkyl cycloheptanes. All of the possible alkyl cyclopentanes normally boiling up to 132°C have been isolated, except for three compounds which are believed to be present only in extremely small amounts. All of the possible alkyl cyclohexanes normally boiling up to 132°C, including one $C_6$, one $C_7$, and eight $C_8$ compounds, have been isolated. In addition, three of the $C_9$ trimethylcyclohexanes have been isolated. Among the alkyl cycloheptanes, only cycloheptane itself, present in very small amounts, has been isolated to date. So far four bicycloparaffins have been isolated from the gasoline fraction. All of the 21 possible mononuclear aromatics have been isolated from this gasoline fraction. Of these, 20 are alkyl benzenes and one is an aromatic-cycloparaffin indan.

*Kerosine.* The hydrocarbons of this fraction, taken as the material normally boiling from 180° to 230°C, consist of normal ($C_{11}$ and $C_{12}$) and branched paraffins, mono-, bi-, and higher cycloparaffins, and mono- and dinuclear aromatics. From this material have been isolated two normal paraffins, one alkyl cyclohexane, six bicycloparaffins, one tricycloparaffin (adamantane), 20 alkyl benzenes, six aromatic-cycloparaffins, and one dinuclear aromatic, as listed in Table 4.

*Light Gas Oil.* The hydrocarbons of this fraction, taken as the material normally boiling from 230° to 305° C, consist of normal ($C_{13}$ to $C_{17}$) and branched paraffins, mono-, bi-, and higher cycloparaffins, and mono- and dinuclear aromatics. From this have been isolated five normal paraffins, one aromatic-cycloparaffin, and six dinuclear aromatics, listed in Table 4.

*Heavy Gas Oil and Light Lubricating Distillate.* The hydrocarbons of this fraction, taken as the material normally boiling from 305° to 405°C, consist of normal ($C_{18}$ to $C_{25}$) and branched paraffins, mono-, bi-, and higher cycloparaffins, and mono-, di-, and higher nuclear aromatics. From this material, ten hydrocarbons have been isolated, including eight normal paraffins, one dinuclear aromatic, and one trinuclear aromatic, as listed in Table 4.

*Lubricant.* The hydrocarbons of this fraction, taken as the material normally boiling from 405° to 515°C, consist of normal ($C_{26}$ to $C_{38}$) and branched paraffins, mono-, bi-, and higher cycloparaffins, and mono-, di-, and higher nuclear aromatics. From this material, only seven normal paraffins have been isolated, as given in Table 4.

### Types of Homologs

*Normal Paraffins.* As indicated earlier, all of the normal paraffins, $C_1$ to $C_{33}$, have been isolated. The amount of each in the original petroleum, in per cent by volume, increases from 1.8 for $C_6$ to 2.3 for $C_7$ and then decreases gradually to an estimated value of 0.09 for $C_{33}$.

*Branched Paraffins.* A total of 37 branched paraffins have been isolated, all from the gas and gasoline fractions. Enough has been learned about this class to indicate that all possible isomers may be present, although many only in trace amounts. The most abundant isomer in any group is usually the 2-methyl isomer, with the 3-methyl and 4-methyl isomers following. In any given group of isomers, the bulk of the material will consist of the singly branched isomers with the amounts of the doubly-branched ones dropping sharply and of the triply-branched ones even more so. For example, in this representative

Table 3. Distribution, by Class and Number of Carbon Atoms per Molecule, of the Hydrocarbons Isolated

| Number of carbon atoms per molecule | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | Total |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Branched paraffins | 1 | 1 | 4 | 6 | 15 | 7 | 3 | ... | ... | ... | ... | 37 |
| Alkyl cyclopentanes | ... | 1 | 1 | 5 | 13 | 2 | ... | ... | ... | ... | ... | 22 |
| Alkyl cyclohexanes | ... | ... | 1 | 1 | 8 | 3 | 1 | ... | ... | ... | ... | 14 |
| Alkyl cycloheptanes | ... | ... | ... | 1 | ... | ... | ... | ... | ... | ... | ... | 1 |
| Bicycloparaffins | ... | ... | ... | ... | 3 | 1 | 5 | 1 | ... | ... | ... | 10 |
| Tricycloparaffins | ... | ... | ... | ... | ... | ... | 1 | ... | ... | ... | ... | 1 |
| Alkyl benzenes | ... | ... | 1 | 1 | 4 | 8 | 22 | 4 | ... | ... | ... | 40 |
| Aromatic cycloparaffins | ... | ... | ... | ... | ... | 1 | 4 | 3 | ... | ... | ... | 8 |
| Dinuclear aromatics | ... | ... | ... | ... | ... | ... | 1 | 2 | 3 | 1 | 1 | 8 |
| Trinuclear aromatics | ... | ... | ... | ... | ... | ... | ... | ... | ... | ... | 1 | 1 |
| Total | 1 | 2 | 7 | 14 | 43 | 21 | 37 | 10 | 3 | 1 | 2 | 142 |
| Normal paraffins, $C_1$ to $C_{33}$ | | | | | | | | | | | | 33 |
| Grand total | | | | | | | | | | | | 175 |

## Table 4. Hydrocarbons in the Representative Petroleum of the API Research Project 6

| Formula | Compound | Normal boiling point (°C) | Amount[a] (percentage by volume) |
|---|---|---|---|
| | *Normal paraffins* | | |
| $CH_4$ | Methane | −161.49 | (0.1) |
| $C_2H_6$ | Ethane | − 88.63 | (0.2) |
| $C_3H_8$ | Propane | − 42.07 | (0.4) |
| $C_4H_{10}$ | *n*-Butane | − 0.50 | (0.9) |
| $C_5H_{12}$ | *n*-Pentane | 36.07 | (1.6) |
| $C_6H_{14}$ | *n*-Hexane | 68.74 | 1.8 |
| $C_7H_{16}$ | *n*-Heptane | 98.43 | 2.3 |
| $C_8H_{18}$ | *n*-Octane | 125.66 | 1.9 |
| $C_9H_{20}$ | *n*-Nonane | 150.80 | 1.8 |
| $C_{10}H_{22}$ | *n*-Decane | 174.12 | 1.8 |
| $C_{11}H_{24}$ | *n*-Undecane | 195.89 | 1.6 |
| $C_{12}H_{26}$ | *n*-Dodecane | 216.28 | 1.4 |
| $C_{13}H_{28}$ | *n*-Tridecane | 235.43 | 1.2 |
| $C_{14}H_{30}$ | *n*-Tetradecane | 253.52 | 1.0 |
| $C_{15}H_{32}$ | *n*-Pentadecane | 270.61 | 0.8 |
| $C_{16}H_{34}$ | *n*-Hexadecane | 286.79 | 0.7 |
| $C_{17}H_{36}$ | *n*-Heptadecane | 302.15 | 0.6 |
| $C_{18}H_{38}$ | *n*-Octadecane | 316.71 | 0.50 |
| $C_{19}H_{40}$ | *n*-Nonadecane | 330.6 | 0.43 |
| $C_{20}H_{42}$ | *n*-Eicosane | 343.8 | 0.37 |
| $C_{21}H_{44}$ | *n*-Heneicosane | 356.5 | 0.32 |
| $C_{22}H_{46}$ | *n*-Docosane | 368.6 | 0.28 |
| $C_{23}H_{48}$ | *n*-Tricosane | 380.2 | 0.25 |
| $C_{24}H_{50}$ | *n*-Tetracosane | 391.3 | 0.22 |
| $C_{25}H_{52}$ | *n*-Pentacosane | 401.9 | 0.20 |
| $C_{26}H_{54}$ | *n*-Hexacosane | 412.2 | (0.18) |
| $C_{27}H_{56}$ | *n*-Heptacosane | 422.1 | (0.16) |
| $C_{28}H_{58}$ | *n*-Octacosane | 431.6 | (0.14) |
| $C_{29}H_{60}$ | *n*-Nonacosane | 440.8 | (0.13) |
| $C_{30}H_{62}$ | *n*-Triacontane | 449.7 | (0.12) |
| $C_{31}H_{64}$ | *n*-Hentriacontane | 458.0 | (0.11) |
| $C_{32}H_{66}$ | *n*-Dotriacontane | 467.0 | (0.10) |
| $C_{33}H_{68}$ | *n*-Tritriacontane | 475.0 | (0.09) |
| | *Branched paraffins* | | |
| $C_4H_{10}$ | 2-Methylpropane (isobutane) | − 11.73 | (0.3) |
| $C_5H_{12}$ | 2,2-Dimethylpropane (neopentane) | 9.50 | [b] |
| " | 2-Methylbutane (isopentane) | 27.85 | (0.5) |
| $C_6H_{14}$ | 2,2-Dimethylbutane | 49.74 | 0.04 |
| " | 2,3-Dimethylbutane | 57.99 | 0.08 |
| " | 2-Methylpentane | 60.27 | 0.37 |
| " | 3-Methylpentane | 63.28 | 0.35 |
| $C_7H_{16}$ | 2,2-Dimethylpentane | 79.20 | 0.02 |
| " | 2,4-Dimethylpentane | 80.50 | 0.08 |
| " | 2,2,3-Trimethylbutane | 80.87 | [b] |
| " | 3,3-Dimethylpentane | 86.07 | [b] |
| " | 2,3-Dimethylpentane | 89.78 | 0.15 |
| " | 2-Methylhexane | 90.05 | 0.73 |
| " | 3-Methylhexane | 91.85 | 0.51 |
| " | 3-Ethylpentane | 93.48 | 0.06 |
| $C_8H_{18}$ | 2,2,4-Trimethylpentane | 99.24 | [b] |
| " | 2,2,3,3-Tetramethylbutane | 106.47 | [b] |
| " | 2,2-Dimethylhexane | 106.84 | 0.01 |
| " | 2,5-Dimethylhexane | 109.10 | 0.06 |
| " | 2,4-Dimethylhexane | 109.43 | 0.06 |
| " | 2,2,3-Trimethylpentane | 109.84 | 0.004 |
| " | 3,3-Dimethylhexane | 111.97 | 0.03 |
| " | 2,3,4-Trimethylpentane | 113.47 | 0.005 |
| " | 2,3,3-Trimethylpentane | 114.76 | 0.006 |
| " | 2,3-Dimethylhexane | 115.61 | 0.07 |
| " | 2-Methyl-3-ethylpentane | 115.65 | 0.06 |
| " | 2-Methylheptane | 117.65 | 0.90 |
| " | 4-Methylheptane | 117.71 | 0.20 |
| " | 3,4-Dimethylhexane | 117.72 | 0.13 |
| " | 3-Methyl-3-ethylpentane | 118.26 | 0.02 |
| " | 3-Ethylhexane | 118.53 | 0.09 |
| " | 3-Methylheptane | 118.92 | 0.30 |
| $C_9H_{20}$ | 2,2,4,4-Tetramethylpentane | 122.28 | [b] |
| " | 2,2,5-Trimethylhexane | 124.08 | 0.002 |
| " | 2,2,4-Trimethylhexane | 126.54 | [b] |
| " | 2,3,5-Trimethylhexane | 131.34 | 0.03 |
| " | 2,6-Dimethylheptane | 135.21 | 0.05 |
| " | 2,3-Dimethylheptane | 140.5 | 0.05 |
| " | 4-Methyloctane | 142.48 | 0.1 |
| " | 2-Methyloctane | 143.26 | 0.4 |
| " | 3-Methyloctane | 144.18 | 0.1 |
| $C_{10}H_{22}$ | 5-Methylnonane | 165.1 | [b] |
| " | 4-Methylnonane | 165.7 | 0.1 |
| " | 2-Methylnonane | 166.8 | 0.3 |
| " | 3-Methylnonane | 167.8 | 0.1 |
| | *Alkyl cyclopentanes* | | |
| $C_5H_{10}$ | Cyclopentane | 49.26 | 0.05 |
| $C_6H_{12}$ | Methylcyclopentane | 71.81 | 0.87 |
| $C_7H_{14}$ | 1,1-Dimethylcyclopentane | 87.85 | 0.16 |
| " | 1,cis-3-Dimethylcyclopentane | 90.77 | 0.87 |
| " | 1,trans-3-Dimethylcyclopentane | 91.72 | 0.21 |
| " | 1,trans-2-Dimethylcyclopentane | 91.87 | 0.48 |
| " | 1,cis-2-Dimethylcyclopentane | 99.53 | [b] |
| " | Ethylcyclopentane | 103.47 | 0.16 |
| $C_8H_{16}$ | 1,1,3-Trimethylcyclopentane | 104.89 | 0.30 |
| " | 1,trans-2,cis-4-Trimethylcyclopentane | 109.29 | 0.22 |
| " | 1,trans-2,cis-3-Trimethylcyclopentane | 110.2 | 0.26 |
| " | 1,1,2-Trimethylcyclopentane | 113.73 | 0.06 |
| " | 1,cis-2,trans-4-Trimethylcyclopentane | 116.73 | 0.01 |
| " | 1,cis-2,trans-3-Trimethylcyclopentane | 117.5 | 0.07 |
| " | 1,cis-2,cis-4-Trimethylcyclopentane | 118. | [b] |
| " | 1-Methyl-trans-3-ethylcyclopentane | 120.8 | 0.12 |
| " | 1-Methyl-cis-3-ethylcyclopentane | 121.4 | |

| Formula | Compound | Normal boiling point (°C) | Amount[a] (percentage by volume) |
|---|---|---|---|
| | *Alkyl cyclopentanes* | | |
| $C_8H_{16}$ | 1-Methyl-trans-2-ethylcyclopentane | 121.2 | 0.14 |
| " | 1-Methyl-1-ethylcyclopentane | 121.52 | 0.03 |
| " | 1-cis-2,cis-3-Trimethylcyclopentane | 123.0 | [b] |
| " | Isopropylcyclopentane | 126.42 | 0.01 |
| " | 1-Methyl-cis-2-ethylcyclopentane | 128.05 | 0.04 |
| " | *n*-Propylcyclopentane | 130.95 | 0.06 |
| $C_9H_{18}$ | 1,1,3,3-Tetramethylcyclopentane | 117.96 | [b] |
| " | 1,1,cis-3,trans-4-Tetramethylcyclopentane | 121.6 | 0.04 |
| " | 1,trans-2,cis-3,trans-4-Tetramethylcyclopentane | 127.4 | 0.11 |
| " | 1,1,cis-2,trans-3-Tetramethylcyclopentane | 130. | [b] |
| " | 1,1,cis-2,cis-3-Tetramethylcyclopentane | 130. | [b] |
| " | 1,1,cis-2,trans-4-Tetramethylcyclopentane | 130. | [b] |
| " | 1,cis-2,trans-3,cis-4-Tetramethylcyclopentane | 131. | [b] |
| " | 1,trans-2,trans-3,cis-4-Tetramethylcyclopentane | 131. | [b] |
| $C_6H_{12}$ | Cyclohexane | 80.74 | 0.71 |
| $C_7H_{14}$ | Methylcyclohexane | 100.93 | 1.6 |
| $C_8H_{16}$ | 1,trans-4-Dimethylcyclohexane | 119.35 | 0.25 |
| " | 1,1-Dimethylcyclohexane | 119.54 | 0.06 |
| " | 1,cis-3-Dimethylcyclohexane | 120.09 | 0.63 |
| " | 1,trans-2-Dimethylcyclohexane | 123.42 | 0.31 |
| " | 1,cis-4-Dimethylcyclohexane | 124.32 | 0.09 |
| " | 1,trans-3-Dimethylcyclohexane | 124.45 | 0.07 |
| " | 1,cis-2-Dimethylcyclohexane | 129.73 | 0.06 |
| " | Ethylcyclohexane | 131.78 | 0.37 |
| $C_9H_{18}$ | 1,1,3-Trimethylcyclohexane | 136.63 | 0.2 |
| " | 1,trans-2,trans-4-Trimethylcyclohexane | 141.22 | 0.2 |
| " | 1,trans-2,cis-4-Trimethylcyclohexane | 145.6 | (0.1) |
| $C_{10}H_{20}$ | *n*-Butylcyclohexane | 180.95 | (0.22) |
| | *Cycloheptanes* | | |
| $C_7H_{14}$ | Cycloheptane | 118.79 | 0.01 |
| | *Bicycloparaffins* | | |
| $C_8H_{14}$ | Methylbicyclo-[2.2.1]-heptane | 124.5 | 0.001 |
| " | cis-Bicyclo-[3.3.0]-octane | 136.5 | 0.06 |
| " | Bicyclo-[3.2.1]-octane | (138.) | 0.008 |
| $C_9H_{16}$ | Bicycloparaffin[c] | 146.7 | (0.06) |
| $C_{10}H_{18}$ | Bicycloparaffin[c] | 180. | (0.01) |
| " | Bicycloparaffin[c] | 183.4 | (0.01) |
| " | Bicycloparaffin[c] | 183.7 | (0.02) |
| " | trans-Bicyclo-[4.4.0]-decane (trans-Decahydronaphthalene) | 187.25 | (0.2) |
| " | cis-Bicyclo-[4.4.0]-decane (cis-Decahydronaphthalene) | 195.69 | (0.01) |
| $C_{11}H_{20}$ | Bicycloparaffin[c] | 202.5 | (0.12) |
| | *Tricycloparaffins* | | |
| $C_{10}H_{16}$ | Tricyclo-[3.3.1.1$^{3,7}$]-decane (Adamantane) | 190. | 0.0004 |
| | *Alkyl benzenes* | | |
| $C_6H_6$ | Benzene | 80.10 | 0.15 |
| $C_7H_8$ | Methylbenzene (toluene) | 110.62 | 0.51 |
| $C_8H_{10}$ | Ethylbenzene | 136.19 | 0.19 |
| " | 1,4-Dimethylbenzene (*p*-Xylene) | 138.35 | 0.10 |
| " | 1,3-Dimethylbenzene (*m*-Xylene) | 139.10 | 0.51 |
| " | 1,2-Dimethylbenzene (*o*-Xylene) | 144.41 | 0.27 |
| $C_9H_{12}$ | Isopropylbenzene | 152.39 | 0.07 |
| " | *n*-Propylbenzene | 159.22 | 0.09 |
| " | 1-Methyl-3-ethylbenzene | 161.30 | 0.17 |
| " | 1-Methyl-4-ethylbenzene | 161.99 | 0.06 |
| " | 1,3,5-Trimethylbenzene | 164.72 | 0.12 |
| " | 1-Methyl-2-ethylbenzene | 165.15 | 0.09 |
| " | 1,2,4-Trimethylbenzene | 169.35 | 0.51 |
| " | 1,2,3-Trimethylbenzene | 176.08 | 0.19 |
| $C_{10}H_{14}$ | tert-Butylbenzene | 169.12 | 0.01 |
| " | Isobutylbenzene | 172.76 | 0.008 |
| " | sec-Butylbenzene | 173.30 | 0.017 |
| " | 1-Methyl-3-isopropylbenzene | 175.14 | 1.08 |
| " | 1-Methyl-4-isopropylbenzene | 177.10 | 0.04 |
| " | 1-Methyl-2-isopropylbenzene | 178.15 | 0.009 |
| " | 1,3-Diethylbenzene | 181.10 | 0.029 |
| " | 1-Methyl-3-propylbenzene | 181.80 | 0.059 |
| " | *n*-Butylbenzene | 183.27 | 0.026 |
| " | 1-Methyl-4-propylbenzene | 183.30 | 0.027 |
| " | 1,2-Diethylbenzene | 183.42 | 0.005 |
| " | 1,3-Dimethyl-5-ethylbenzene | 183.58 | 0.063 |
| " | 1,4-Diethylbenzene | 183.78 | 0.007 |
| " | 1-Methyl-2-propylbenzene | 184.80 | 0.046 |
| " | 1,4-Dimethyl-2-ethylbenzene | 186.83 | 0.041 |
| " | 1,3-Dimethyl-3-ethylbenzene | 188.20 | 0.050 |
| " | 1,2-Dimethyl-4-ethylbenzene | 189.48 | 0.057 |
| " | 1,3-Dimethyl-2-ethylbenzene | 190.01 | 0.014 |
| " | 1,2-Dimethyl-3-ethylbenzene | 193.91 | 0.03 |
| " | 1,2,4,5-Tetramethylbenzene | 196.80 | 0.052 |
| " | 1,2,3,5-Tetramethylbenzene | 198.00 | 0.1 |
| " | 1,2,3,4-Tetramethylbenzene | 205.04 | 0.2 |
| $C_{11}H_{16}$ | 1-Methyl-3-*n*-butylbenzene | 204.1 | 0.06 |
| " | 1,3-Dimethyl-4-*n*-propylbenzene | 206.6 | 0.03 |
| " | 1,2-Dimethyl-4-*n*-propylbenzene | 208.5 | 0.03 |
| " | Trimethylethylbenzene | 212.3 | 0.04 |

[a] The figures in parentheses are less certain than the others. Where no value is given for a compound, it is implied that the compound listed is believed to be present in very small amount, less than was detectable at the time the given material was investigated.

[b] Believed to be present in extremely small amount.

[c] Not yet identified.

**Table 4 (continued)**

| Formula | Compound | Normal boiling point (°C) | Amounts (percentage by volume) |
|---|---|---|---|
| | *Aromatic-cycloparaffins* | | |
| $C_9H_{10}$ | Indan | 177.8 | 0.003 |
| $C_{10}H_{12}$ | 1-Methylindan | 190.6 | 0.022 |
| " | 2-Methylindan | 191.4 | |
| " | 4-Methylindan | 205.5 | (0.03) |
| " | 1,2,3,4-Tetrahydronaphthalene | 207.57 | 0.03 |
| $C_{11}H_{14}$ | 2-Methyl-1,2,3,4-tetrahydronaphthalene | 220.7 | 0.04 |
| " | 6-Methyl-1,2,3,4-tetrahydronaphthalene | 229.3 | 0.09 |
| " | 5-Methyl-1,2,3,4-tetrahydronaphthalene | 234.35 | 0.08 |
| | *Dinuclear aromatics* | | |
| $C_{10}H_8$ | Naphthalene | 217.96 | 0.06 |
| $C_{11}H_{10}$ | 2-Methylnaphthalene | 241.05 | 0.2 |
| " | 1-Methylnaphthalene | 244.64 | 0.1 |
| $C_{12}H_{12}$ | Biphenyl | 255.2 | (0.03) |
| " | 2,6-Dimethylnaphthalene | 262. | (0.35) |
| " | Dimethylnaphthalene[c] | 268. | (0.35) |
| $C_{13}H_{14}$ | Trimethylnaphthalene[c] | 288. | (0.20) |
| $C_{14}H_{14}$ | Alkyl naphthalene[c] | 312. | (0.20) |
| | *Trinuclear aromatics* | | |
| $C_{14}H_{10}$ | Phenanthrene | 340. | (0.20) |

[c] Not yet identified.

petroleum, the amounts of each of the $C_9$ branched isomers, are, in per cent, of the following orders: singly-branched, 0.1; doubly-branched, 0.01; triply-branched, 0.001; quadruply-branched, trace. Knowing (*a*) the total amount of the branched paraffins of a given carbon number, through analysis by type of the broad fractions, (*b*) the number of isomers which are singly-branched, doubly-branched, etc., and (*c*) the relative amounts of the compounds of different branching, it is thus possible to estimate the order of magnitude of the amount of any given branched paraffin in petroleum.

*Monocycloparaffins.* Most of the monocycloparaffins in petroleum are alkyl cyclopentanes and alkyl cyclohexanes, with only a small amount of alkyl cycloheptanes. In general, in a given group of isomers of the alkyl cyclopentanes, the most abundant compounds are those with the largest number of substituents, each on a different carbon atom, with the substituents on adjacent carbon atoms being "trans" to one another. Similarly, in a given group of isomers of the alkyl cyclohexanes, the most abundant compounds are those with the largest number of substituents, each on a different carbon atom, with the substituents being "equatorial" rather than "axial" to minimize steric hindrance in the molecules. These are also the isomers which are thermodynamically more stable. One interesting structure, related to other natural products occurring among the monocycloparaffins, is found in 1,1,3-trimethylcyclopentane and in 1,1,3-trimethylcyclohexane, both relatively abundant in petroleum.

*Bicycloparaffins.* So far, ten bicycloparaffins have been isolated, four from the gasoline fraction and six from the kerosine fraction. In Figure 2 are shown the structures of the nuclei of bicycloparaffin hydrocarbons believed to be the ones occurring in petroleum in significant amount. As may be noted, these are structures which have five or six carbon atoms in each ring, a carbon common to two rings being counted twice. The numbering system is the approved one, with the numbers representing the number of carbon atoms in each bridge.

*Mononuclear Aromatics.* As may be seen from Table 4, all of the 32 possible aromatic hydrocarbons normally boiling up to 190°C have been isolated from this petroleum. Sixteen additional mononuclear aromatics have also been isolated. In any given group of isomers, the alkyl benzenes which are most abundant are those which are thermodynamically more stable, as the 1,3-dialkyl or 1,2,4-trialkyl benzenes, with less preference for the 1,2-dialkyl benzenes. Also, in a given group, the compounds with more substituents are more abundant, as 1,2,4-trimethylbenzene is more abundant than 1-methyl-3-ethylbenzene. With increase in the number of carbon atoms, more of the mononuclear aromatics will be of the aromatic-cycloparaffin subclass, in which, generally, the benzene ring is joined through two common carbon atoms to a cyclopentane ring or a cyclohexane ring or multi-ring combinations of these.

*Dinuclear aromatics.* A total of eight dinuclear aromatics have been isolated, including naphthalene, biphenyl, and six alkyl naphthalenes. The alkyl naphthalenes are much more abundant than the alkyl biphenyls. With increasing number of carbon atoms per molecule, the dinuclear aromatics will include an increasing number of aromatic cycloparaffins, with the naphthalene nucleus attached through two common carbon atoms to a mono- or bi- or higher cycloparaffin group.

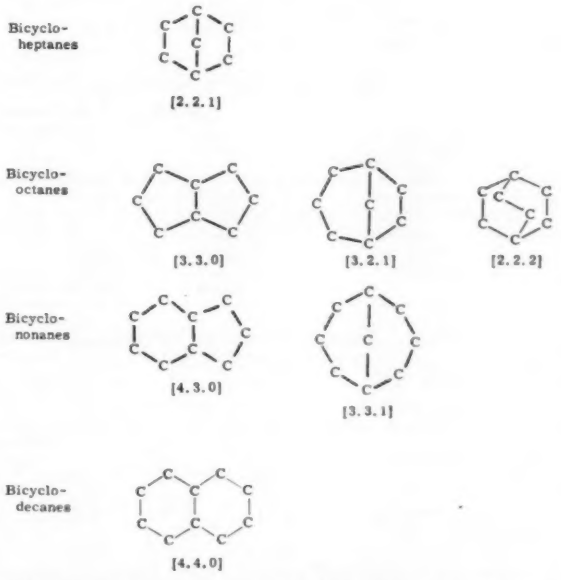


**Figure 2. Structures of the nuclei of bicycloparaffin hydrocarbons believed to be the ones occurring in petroleum in significant amounts.**

*Higher Nuclear Aromatics.* Only one compound of this group has so far been isolated, the trinuclear aromatic, phenanthrene. The alkyl phenanthrenes are expected to be more abundant than the alkyl anthracenes. Also, among the higher nuclear aromatics will occur many aromatic-cycloparaffin compounds, with the cycloparaffin portion consisting of several rings, generally condensed together with the aromatic nucleus.

### Composition of Petroleums in General

Some years ago, the API Research Project 6 completed a study of the hydrocarbons from different petroleums (*13*, *21*). The Project's one representative petroleum from Oklahoma was intermediate in type. The gasoline fractions from six additional representative petroleums were selected to represent large production in different areas of the United States and to be as different as was known at the time.

The seven representative gasoline fractions were as follows, with the type and source field: A, intermediate, Ponca, Oklahoma; B, intermediate, East Texas; C, high in paraffins, Bradford, Pennsylvania; D, high in normal paraffins, Greendale-Kawkawlin, Michigan; E, high in branched paraffins, Winkler, Texas; F, high in cycloparaffins, Midway, California; G, high in aromatics, Conroe, Texas.

By means of an extended but relatively short procedure involving the fractionating processes of adsorption and distillation, both operated at high separating power, analyses were made of the major paraffin and cycloparaffin components in the 40° to 102°C range of these gasolines and of the alkyl benzenes to 180°C. From this work, the following conclusions were reached:

All petroleums contain substantially the same hydrocarbon compounds.

The principal compounds in the gasoline fraction of each petroleum may be placed in five main classes: normal (straight-chain) paraffins; branched paraffins; alkyl cyclopentanes; alkyl cyclohexanes; alkyl benzenes.

Within each of these five classes, the individual compounds occur in proportions which are usually of the same order of magnitude for different petroleums.

Table 5 gives the relative amounts of the five main classes of hydrocarbons in the 40° to 102°C fraction of the seven petroleums, with the letters, A, B, C, D, E, F, and G representing the same petroleums as above. These figures indicate considerable variation in the relative amounts of the several classes from one petroleum to the other. For example, the ratio of normal paraffins to branched paraffins ranges from 4.8 for D to 0.15 for E, a variation of over 30-fold. Similarly, the ratio of alkyl cyclopentanes to alkyl benzenes ranges from 68 for F to 4.6 for G, a variation of 14-fold.

Table 6 shows how the relative amounts of individual compounds within given classes have nearly the same values in the different gasolines, taking three examples: (1) The relative amounts of benzene, toluene, and the four $C_8$ alkyl benzenes; (2) the relative amounts of cyclohexane and methylcyclohexane; (3) the relative amounts of the two methylpentanes and the two dimethylbutanes. Additional similar examples may be cited. It is to be noted that the actual amount of the compounds considered varies considerably from one gasoline to another, as indicated by the bottom row of figures for each group of compounds in Table 6.

These results mean that the exhaustive information and data being obtained on the Project's one representative petroleum can be readily translated to other petroleums by making some relatively simple observations on the other petroleums. Although the work on other petroleums has been limited to the gasoline fractions, it is quite clear that the same principles may be applied to compounds of the same class in

**Table 5. Relative Amounts of the Main Classes of Hydrocarbons in the 40–102°C Fraction of the Seven Representative Gasolines**

| Type of gasoline → Class of hydrocarbons | A | B | C | D | E | F | G |
|---|---|---|---|---|---|---|---|
| | Relative amount by volume | | | | | | |
| Normal paraffins | 35.3 | 24.6 | 34.1 | 62.2 | 9.5 | 9.9 | 17.6 |
| Branched paraffins | 20.2 | 27.1 | 32.0 | 13.0 | 61.4 | 21.4 | 19.6 |
| Alkyl cyclopentanes | 23.1 | 25.9 | 13.4 | 7.8 | 20.4 | 40.7 | 16.6 |
| Alkyl cyclohexanes | 20.2 | 21.9 | 20.0 | 15.5 | 8.2 | 27.4 | 42.6 |
| Alkyl benzenes | 1.2 | 0.5 | 0.5 | 1.5 | 0.5 | 0.6 | 3.6 |
| Total | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 | 100.0 |

**Table 6. Relative Amounts of Individual Compounds within Given Classes in the Seven Different Gasolines**

| Type of gasoline → Compounds | A | B | C | D | E | F | G | Range of relative amount | Average relative amount |
|---|---|---|---|---|---|---|---|---|---|
| | | | | *Alkyl benzenes, $C_8$ to $C_9$* | | | | | |
| Relative amounts | | | | | | | | | |
| Benzene | 0.09 | 0.04 | 0.04 | 0.13 | 0.10 | 0.05 | 0.06 | 0.04–0.13 | 0.07 |
| Toluene | 0.30 | 0.29 | 0.31 | 0.37 | 0.20 | 0.30 | 0.38 | 0.20–0.38 | 0.31 |
| $C_8$ alkyl benzenes | 0.61 | 0.67 | 0.65 | 0.50 | 0.70 | 0.65 | 0.56 | 0.50–0.70 | 0.62 |
| Percentage of the gasoline fractio constituted byn this compound | 5.4 | 5.9 | 4.9 | 4.8 | 1.3 | 4.3 | 19.5 | ... | ... |
| | | | | *Alkyl cyclohexanes, $C_6$ and $C_7$* | | | | | |
| Relative amounts | | | | | | | | | |
| Cyclohexane | 0.30 | 0.21 | 0.24 | 0.33 | 0.31 | 0.29 | 0.30 | 0.21–0.33 | 0.28 |
| Methylcyclohexane | 0.70 | 0.79 | 0.76 | 0.67 | 0.69 | 0.71 | 0.70 | 0.67–0.79 | 0.72 |
| Percentage of the gasoline fraction constituted by this compound | 6.9 | 8.4 | 7.3 | 6.1 | 2.1 | 8.4 | 13.7 | ... | ... |
| | | | | *Branched paraffins, $C_6$* | | | | | |
| Relative amounts | | | | | | | | | |
| Dimethylbutanes | 0.14 | 0.13 | 0.10 | 0.14 | 0.12 | 0.16 | 0.16 | 0.10–0.16 | 0.14 |
| Methylpentanes | 0.86 | 0.87 | 0.90 | 0.86 | 0.88 | 0.84 | 0.84 | 0.84–0.90 | 0.86 |
| Percentage of the gasoline fraction constituted by this compound | 2.6 | 4.8 | 6.0 | 2.6 | 6.6 | 3.4 | 3.1 | ... | ... |

the higher-boiling fractions. For example, the relative amounts found in the Project's representative petroleum for naphthalene, 1-methylnaphthalene, and 2-methylnaphthalene are expected to be of the same magnitude for other petroleums; namely, approximately 1 to 2 to 4. Similarly, the ratio of tert-butylbenzene to 1,2,4-trimethylbenzene (pseudocumene) can be expected to be about 1 to 50 approximately, in all petroleums.

A more complete separation of the petroleum into subclasses would be:

The monocycloparaffins separated into (1) alkyl cyclopentanes and (2) alkyl cyclohexanes.

The mononuclear aromatics separated into (1) alkyl benzenes and (2) aromatic cycloparaffins.

The dinuclear aromatics separated into (1) alkyl naphthalenes and (2) aromatic cycloparaffins.

If this additional separation could be performed, say on the gasoline, kerosine, and light gas oil fractions, one would be led to the following statement: An aliquot sample of all the hydrocarbons of any one subclass from one of these broad fractions, gasoline, kerosine, and light gas oil, will be substantially the same for different petroleums with respect to the magnitude of the individual compounds in the sample. That is to say, for example, a liter of all the branched paraffins from the kerosine fraction of one petroleum will be substantially the same as a liter of all the branched paraffins from the same kerosine fraction of another petroleum. Similarly, a liter of all the alkyl naphthalenes from the light gas oil fraction of one petroleum will be substantially the same as a liter of all the alkyl naphthalenes from the same light gas oil fraction of another petroleum.

## Conclusion

In the past 30 years, we have come a long way in our knowledge of what petroleum is chemically. However, we still have facing us several very important scientific questions concerning petroleum, as follows:

How did petroleum get to be *what* it is chemically?

How did petroleum get to be *where* we find it in the earth?

Was petroleum made by nature in one fell swoop, once for all time, or is it being made in the earth continuously?

Because there are numerous investigators working in many different laboratories seeking to uncover these secrets of nature, we are confident that in a few years we will have some answers to these important questions.

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# Jaroslav Heyrovsky: Nobel Laureate

The 1959 Nobel Prize in Chemistry was awarded to Professor Jaroslav Heyrovsky of Czechoslovakia for his discovery of polarography and for his role in the development of this technique which has become such an important theoretical and practical tool in electrochemistry, analytical chemistry, and many other areas of science and technology.

Although most chemists are acquainted with Heyrovsky's name, few know much about his life and personality. The purposes of the present paper are to reveal him as a man and as a chemist, and to indicate in some measure why the award of the Nobel Prize to him was so widely acclaimed as a most justified reward.

## The Role of Polarography in Chemistry

It is interesting to note that whereas many physical methods were brought to an applicable form by the joint or independent efforts of a number of scientists with sometimes even the attribution of priority being questionable, the discovery of polarography is the achievement of one person, even though the development of the method was effected by the efforts of many individuals, including pupils, co-workers, and friends.

The connection of polarography and its originator is unusual in the annals of science. It is rare that a discoverer of a scientific approach is able to force the expansion of the method he developed towards the world-wide reception accorded polarography. It is furthermore rather exceptional that a man should be able to remain for almost forty years among the top investigators in a field which he first opened: a field whose magnitude is indicated by the approximately nine hundred papers published each year which deal with polarography.

With some important experimental approaches, considerable periods of time have elapsed between the discovery of the physical effect and its extensive practical application, e.g., over a century passed after the discovery of infrared spectra at the beginning of the nineteenth century before the method was used for the study of the structure of organic compounds. Polarography, on the other hand, found rapid application and within 20 years of its discovery was extensively used.

Polarography is currently one of the most frequently applied methods of analytical chemistry (*1*) both in research laboratories and in production control. The first field of broad practical application was metallurgy, where the speed and sensitivity of polarographic methods were early appreciated. These same advantages were soon recognized in the pharmaceutical industry and in the areas of food chemistry and pollution control. In medicine (*2*), where the method is widely used in clinical analysis, toxicology, and industrial hygiene, another advantage of polarography—the relatively small sample necessary—is also of prime importance; polarography is more extensively used in medicine in Europe than in the U.S.A. Other industries using polarography extensively as a method of both qualitative and quantitative analysis include the heavy chemical industry as well as the petrochemical, photographic, insecticide, rubber, and plastics industries. One of the recent trends in the application of polarography is to the continuous analysis of process streams.

In basic research, polarography has enabled investigators to gain further information on electrode processes, to elucidate their mechanisms, to distinguish chemical reactions preceding and following the electron-transfer process proper, and, in some instances, even to obtain rate constants characterizing some of the steps in such processes. In fact, polarography is sometimes said to have caused a "renaissance" in electrochemistry, e.g., polarographic studies of transport phenomena brought the interest of electrochemists back to important fields of electrochemistry which were supposed to have been "solved" and "closed" in the 1920's.

In other areas of physical chemistry, polarography permits evaluation of thermodynamical constants such as oxidation-reduction potentials and equilibrium constants of chemical reactions in solutions, as well as of such kinetic data as the rate constants of chemical reactions occurring at the electrode surface or in the bulk of the solution.

Polarography has been useful in both inorganic and organic chemistry in the elucidation of reaction mechanisms and equilibria, including the detection of reaction intermediates. Application of polarography often offers a convenient way of choosing the best conditions for synthetic reactions, separations, and isolations. Studies of the correlations between polarographic data and structure and other characteristics of chemical species are of importance not only for the expanding fields of theoretical inorganic, organic, and physical chemistry, but also because they form a sound basis for the initial attempts at using polarography in the elucidation of chemical constitution.

In biochemistry polarography is extensively used both as an analytical tool and for determination of reaction rates and mechanisms of biochemically important reactions; here, the possibilities of selectivity and of continuous measurement, sometimes even in very complicated and turbid solutions, are of importance.

## Heyrovsky and the Development of Polarography

Jaroslav Heyrovsky was born on December 20, 1890, in Prague, where his father was Professor of Roman Law at the Czech University, at that time called Charles-Ferdinand University (see reference *3* for a biography). Interested in mathematics and physics even while attending secondary school, Heyrovsky concentrated on chemistry, physics, and mathematics on entering the University of Prague in 1909. Inspired by the achievements of Sir William Ramsay, he transferred in 1910 to University College in London, where he was mainly influenced by Ramsay's successor, the well-known physical chemist and electrochemist, Professor F. G. Donnan. After attaining the B.Sc. in 1913, Heyrovsky started a doctoral thesis under Donnan's guidance on the determination of the electrode potential of aluminum. Due to the passivity phenomena observed with this metal, Donnan suggested that Heyrovsky use an amalgam dropping electrode similar to that used in Donnan's studies of membrane equilibria in which such an electrode had been used to determine the activity of sodium ion. This was Heyrovsky's introduction to the dropping electrode, a type of electrode which was to persist throughout all of his subsequent scientific career.

These studies were interrupted by World War I. Heyrovsky was home on a visit when war broke out in the summer of 1914. For a few months he was able to continue experimental work at the Chemical Institute of the University of Prague. In January, 1915, he was called up for military service in the Austro-Hungarian army. Due to his delicate physical constitution he spent the major part of his service as a dispensing chemist and roentgenologist in a military hospital. This allowed him to continue work on his thesis, which he submitted in the autumn of 1918 to the University of Prague.

As partial fulfillment for the doctorate degree, Heyrovsky took an examination in physics, which profoundly influenced his scientific career. During the examination, the examiner, Professor B. Kucera, called Heyrovsky's attention to the anomalies of the electrocapillary curves obtained with a dropping mercury electrode in a dilute electrolyte solution and suggested that he study these phenomena. As a result, during the following years, Heyrovsky, who became first an assistant and later the first lecturer (Docent) in physical chemistry at Charles University (1920), spent all of his available time in weighing the mercury, which flowed out of the capillary electrode at different potentials. He also submitted a habilitation thesis on aluminic acid, the constitution of aluminates, and amphoterity; these studies, which were influenced by Professor B. Brauner, resulted in three papers, which enabled Heyrovsky to gain the D.Sc. degree at the University of London in 1921.

Becoming somewhat tired by the troublesome and not always reproducible measurements of electrocapillary curves, Heyrovsky tried to follow the current flowing during the electrolysis between the dropping mercury electrode and a reference electrode. In the course of those experiments, in which the first current-voltage curves were obtained with the dropping mercury electrode, the principles of polarography were discovered. This new approach to the problems of electrolysis was described in papers published in Czech (*4*) and English (*5*), and during the General Discussion on Electrode Reactions and Phenomena, held by the Faraday Society in 1923.

Heyrovsky now devoted all of his time, efforts, and interests to following up his important discovery by studying the electrolytical processes which occur on the tiny mercury drop. He investigated hydrogen overvoltage, using polarographic measurements. With a Japanese collaborator, M. Shikata, he developed in 1925 the polarograph, an instrument for the automatic recording of current-potential, i.e., polarographic, curves. This instrument, which was one of the first examples of automatized laboratory apparatus, avoided the tedious manual point by point measurement of the current-potential curves, and thereby represented a scientific revolution in electrochemistry and chemical analysis. In their paper (*6*) Heyrovsky and Shikata coined the words, "polarograph" for the instrument and "polarography" for the new type of measurement and the new branch of electrochemistry. The names were chosen to emphasize the characteristic role of the polarizing electromotive force in the curves obtained by such measurements.

In 1922 Heyrovsky was appointed assistant professor and was also made the director of the then newly established Department of Physical Chemistry of the Charles University, Prague, which became a center of polarographic research. In 1926 he became professor *ordinarius* of physical chemistry.

After the fundamental experiments with the dropping mercury electrode in the early twenties, Heyrovsky soon recognized the importance of limiting currents. In his laboratory originated the concepts of diffusion-controlled currents (Ilkovic) and of half-wave potentials and their shift with complex-formation, the equation for the polarographic current-potential relation (Heyrovsky-Ilkovic), the existences of migration currents (Heyrovsky, Bures, Kemula), capacity currents (Ilkovic), catalytic currents (Herasymenko, Slendyk, Heyrovsky, Babicka, Brdicka), and many other important contributions to polarographic theory and practice. His co-workers, K. Wiesner and R. Brdicka (Fig. 1), recognized the importance of kinetic-controlled currents in which the electrode reaction is accompanied by a fast

**Figure 1. Professor Brdicka (far left) and Professor Lavfburger, vice president of the Czechoslovak Academy of Science, congratulating Professor Heyrovsky on the occasion of the announcement of the Nobel Prize.**

chemical reaction; Brdicka also first observed and explained adsorption-controlled currents.

The efforts of Professor Heyrovsky to demonstrate the importance and usefulness of polarography were not always easy. For a long period, patience and endurance were necessary before the method was accepted and found its way into chemical laboratories. However, after an induction period of about 10 years, there occurred a steady growth in the number of papers on polarography published annually; the present rate, as mentioned, is about 900 papers yearly. The start of this growth can be traced to a book and two lecture trips, which apparently triggered the world wide dissemination of polarography. The book was a volume of Böttger's treatise (*7*) on physical methods of analysis, which contained a section by Heyrovsky on polarography. In 1933 Heyrovsky lectured on polarography for six months as a Carnegie Visiting Professor at the University of California (Berkeley), Stanford University, and the California Institute of Technology. At the same time, he formed his first links with American scientists by visits to other universities in the central and eastern states. In 1934 Heyrovsky was invited to deliver a lecture on polarography in Leningrad on the occasion of the Mendelejev centenary celebration.

Additional stimulus to the growth of polarography was provided by the visits of students and guests from abroad to Heyrovsky's laboratory. Usually, infected by the enthusiasm of Professor Heyrovsky, they helped to spread the knowledge of polarography throughout the world; many started active centers of research in their home countries, e.g., Shikata in Japan, Kemula in Poland, Breyer in Australia, and Semierano in Italy. From among American chemists, O. H. Müller, now at the State University of New York Medical Center at Syracuse, worked with Professor Heyrovsky for some time and then published an early and influential set of introductory papers on polarography in the JOURNAL OF CHEMICAL EDUCATION in 1941 (*8*), which is now available in revised book form (*9*). An early and influential visitor was I. M. Kolthoff of the University of Minnesota (Fig. 2) who visited Professor Heyrovsky several times before and after World War II, and whose treatise on polarography with J. J. Lingane, now in its second edition (*10*), is the important reference work in the area.

**Figure 2. Dr. Pribil, Dr. Kolthoff, and Dr. Heyrovsky (from left to right) in front of the old building of the Department of Physical Chemistry of Charles University in Prague, where polarography was born.**

## Postwar Scientific Activities

The busy scientific life of the Prague Department of Physical Chemistry was interrupted in 1939 by the Nazis. Although deprived of co-workers and pupils, Heyrovsky was able to continue his work on the expansion of polarography due to the friendly efforts of the German anti-Nazi scientist, Professor J. Bohm, who arranged to have Heyrovsky's laboratory left at his disposal.

**Figure 3. Professor Heyrovsky studying oscillographic curves with his son, Michael.**

In 1941 Heyrovsky began to investigate the oscilloscopic observation of polarographic electrode processes, which enabled him to gather additional information concerning the distinct electrolytic and adsorption processes which occur during the growth of a single mercury drop; this method of investigation has become his principal interest in recent years. Using the $dV/dt - V$ curves obtained at an applied current, Heyrovsky tried mainly to explain the differences in the rates of electrode processes for certain types of depolarizers and the influence of surface-active substances on electrode processes. For these studies, he developed the streaming mercury electrode, which was later successfully used for solving some problems in classical polarography. Professor Heyrovsky explains his interest in "oscillographic polarography" with the statement that a new method always brings new findings and new approaches for the solution of old problems.

After the end of World War II Professor Heyrovsky continued his research activities at the Department of Physical Chemistry with students who were hungry for science after six years of separation from their studies. In 1950 the Polarographic Institute was founded as a state-supported research center; Heyrovsky, who became its first director, left the University, becoming an honorary professor and still delivering lectures on polarography in the Department of Physical Chemistry, now headed by his former pupils M. Kalousek and J. Dvorak. After the reorganization of the Czechoslovak Academy of Sciences in 1952 the

Polarographic Institute was incorporated into the Academy as part of the Chemical Section and one of the Academy's first institutes.

During the 1940's, Professor Heyrovsky became interested in derivative and subtractive differential polarography, which led to further analytical applications of polarography. The last problem in classical polarography which he investigated was, in 1949, the polarography of aldoses in heavy water solution. Recently, he has again become interested in polarographic maxima. These effects which may be due to a stirring of the solution in the neighborhood of the mercury drop also cause the anomalies on the electrocapillary curves, observed by Kucera, which, as indicated earlier, led to the discovery of polarography; this effect is still not yet completely understood.

Another old problem of Heyrovsky's which remains unsolved is that of the polarography of aluminum; this problem is now under study by his son, Michael, who in recent years has helped his father greatly in experimental work (Fig. 3).

The laboratory of Professor Heyrovsky is in an ancient mansion in a quiet street of Prague. The coauthor of this paper, a recent American visitor to Professor Heyrovsky (Fig. 4), described the Polarographic Institute and its director as follows (*11*):

> At the present time the Polarographic Institute, which has grown considerably, is located at two different spots in Prague. The more interesting of these locations is a former palace which has been adapted for use as laboratories. Actually, I was surprised to see how well this has worked out. At the time I was in Prague the building was being completely rewired for an adequate supply of electricity. One pleasant part of the building is the garden which makes a delightful place for discussion. I would guess that there are about 20 people, most of whom are independent professional-level investigators, in this location. The other group has equally well-equipped laboratories on the upper floor of an office building in the center of the city.
>
> I was much impressed by the intellectual vigor of the people in the Institute. They are well informed regarding work in the areas of their interests and enjoy discussing mutual interests. Personally, I found them a most delightful group of people, socially and professionally.
>
> Professor Heyrovsky himself devotes only a minimum amount of time to administrative matters. Most of his time is spent in writing and in personally carrying out laboratory work investigating further developments and applications in the oscillographic presentation of polarographic measurements.
>
> Professor Heyrovsky is obviously very much interested in the young men associated with him in the Academy and encourages their emergence as independent investigators. For example, Professor R. Brdicka (Fig. 1), who was formerly associated with him, is now head of the Institute of Physical Chemistry, another part of the Chemical Section of the Academy.
>
> Professor Heyrovsky is a delightful person with whom to discuss things. It is evident that he keeps up not only with the polarographic literature but with a vast variety of other chemical literature. He remembered with great interest his trip to the United States in 1933 and contrasts the amazing change in the interest in polarography then, when such interest was practically non-existent, with the present interest when polarography is one of the most active fields of investigation in chemistry as is clearly indicated by the large number of papers dealing with polarographic theory, methodology, practice, and applications which are published, for example, each year in the *Journal of the American Chemical Society* and in *Analytical Chemistry*. He is clearly both a scientist and a scholar, as well as a great man in character and in influence.

**Figure 4. Discussion in the Polarographic Institute: Professors Heyrovsky (right) and Elving, 1959.**

## Heyrovsky the Scientist

Posted on the walls of Heyrovsky's laboratories is a quotation from Faraday, "Work, Finish, Publish." In furtherance of this goal, the founder of polarography has always stressed the importance of the printed dissemination of scientific ideas and findings. Besides his more than 170 original scientific papers, Heyrovsky has written a number of review articles as well as several important treatises and textbooks on polarography and derived techniques. The influence of these has already been indicated.

Of primary importance for the extension of the understanding of the polarographic method was his earlier mentioned article on polarographic analysis in Böttger's "Physikalische Methoden der analytischen Chemie (*7*)." It is interesting to note in view of the present-day acceptance of polarography as a standard analytical technique that in 1932, before asking Heyrovsky for a contribution, Böttger, himself a noted analytical chemist, spent a fortnight in Heyrovsky's laboratory to acquaint himself with the method and its analytical importance. Perhaps of even greater scientific influence was Heyrovsky's large textbook, "Polarographie" (*12*), which was published at the same time as the first edition of the monograph by Kolthoff and Lingane, "Polarography" (*13*), which contributed so much to the acceptance of polarography in English-speaking countries. A Russian translation (*14*) of the Czech book on polarography by Heyrovsky's pupil, Varasova, helped to spread a knowledge of polarography in the U.S.S.R.

Professor Heyrovsky has never forgotten that advances in any area of science depend not only on the experienced scientists, but also on the suitable indoctrination of beginners in that area. Consequently, he wrote a detailed elementary laboratory manual (*15*) on polarography which has since been revised (*16*) and published in some eight languages.

More specialized works include one on oscillographic polarography written with Dr. Forejt (*17*), the German edition of which has just appeared with the cooperation of Dr. Kalvoda, and an introduction to theoretical polarography, which is being written with Dr. Kuta.

Early in Heyrovsky's career, it became clear to him that a suitable publication medium for the work of

Czech polarographers and other chemists was urgently needed. In 1928, Heyrovsky and his friend, Professor Votocek, founded an Anglo-French bilingual journal, *Collection of Czechoslovak Chemical Communications;* the journal is now tetralingual (English, German, Russian, French). Until 1947 these two were not only editors of the journal but also its publishers and often the translators of its papers. Most of the polarographic work done in Czechoslovakia has been published in this journal in English or in German.

Professor Heyrovsky also early recognized the importance of systematic documentation work and periodically summarized bibliographical data on polarography in the *Collection of Czechoslovak Chemical Communications.* In the preparations of these bibliographies he has been aided by J. Klumpar (1938) and O. H. Müller (1948–1952); in recent years there has been an unnamed co-author, Mrs. Heyrovsky. These data were first collected in his monographs (*7, 12*) and later (1951) as an independent publication covering the period from 1922 to 1950 (*18*). Since 1951 the "Bibliography of Publications Dealing with the Polarographic Method" has appeared annually as a supplement to the journal. Recently, a subject index to these bibliographies appeared (*19*). Documentation in polarography is thus, as a result of this work and the bibliography (*20*) published by E. H. Sargent and Co. of Chicago, much more accessible than in most other branches of chemistry.

Professor Heyrovsky has always worked very intensively; he still adheres to the habit of spending weekends in the laboratory (in his opinion those are the only days when he is certain not to be disturbed during work). His working day in the Institute is from 8 A.M. to 7 P.M., interrupted only by a short nap after lunch. All of his own studies were and still are made by Heyrovsky without the support of any assistant or technician. He is an excellent example of another motto, found on the walls of the Institute: Newton's "A man must resolve either to produce nothing new or to become a slave to defend it."

Heyrovsky's main interest has always been in the experiment. His strength has consisted of finding new phenomena, of designing new experiments, which enable him to decide among existing ideas, and of being able to distinguish important from unimportant ideas. One of his collaborators compared him to a genial mushroom picker, who is able to find a mushroom even on the highway. He is often ingenious in the explanation of experimental facts, but frequently leaves the more quantitative treatment of the problem to his co-workers. He is fond of theory, but only of theory verified by experiment. When he was the editor of the *Collections,* the journal refused to publish purely theoretical papers without any experimental verification. When Heyrovsky becomes convinced that a theory is in accordance with experiment and explains important findings, he is ready to accept it, admire it, and support it, e.g., his admiration for the work on kinetic currents of his best known co-worker, Professor Brdicka, and the latter's collaborators.

Professor Heyrovsky's scientific success is reflected by the many honors given him. He has been elected to the Czechoslovak Academy of Sciences, the American Academy of Arts and Sciences, and the German, Hungarian, and Indian Academies of Sciences; he is an honorary member of the Czechoslovak, Polish, and Austrian Chemical Societies, of the Society for Analytical Chemistry (England and India), and of the Polarographic Society (London). He has received honorary doctorate degrees from the Universities of Dresden, Warsaw, and Marseilles. He was awarded the Czechoslovak State Prize (1951), the Order of the Czechoslovak Republic (1955), the first Medal of the Polarographic Society (1959), and the Nobel Prize (1959).

Since the end of World War II, Heyrovsky has delivered lectures on one or more occasions in England, Germany, Poland, Austria, the U.S.S.R., Hungary, Sweden, Denmark, Bulgaria, China, and Egypt.

### Heyrovsky the Teacher

It was both the possibility of work in a promising and new field and the personality of Professor Heyrovsky that have attracted so many students and co-workers to him. Heyrovsky's devotion and enthusiasm, his modest and polite behavior, his efforts and patience have made him an outstanding practical example for young people. In his kind manner, he always tries to help anybody interested in polarography. He follows the problems of his pupils just as eagerly as his own, but, when it comes to publication, his name rarely appears on the paper. When it does, more than half of the work has been carried out by him.

Most of his present co-workers in the Polarographic Institute came with him in 1950 from the Department of Physical Chemistry of the Charles University. He does not believe in regulated, forced teamwork, and, consequently, research teams are organized in the Institute only occasionally. Most of the investigators are allowed to choose their own problems, since, in Professor Heyrovsky's opinion, this is the most fruitful approach in basic research. However, when a complex problem is to be solved, the cooperation of specialists in diverse fields is available. At the weekly Institute discussion meetings, no one hesitates to express an opinion, even when it is in disagreement with that of the Director.

Heyrovsky is justly proud of the attachment of his pupils, co-workers, and friends, as reflected, for example, in the numerous letters he receives from all over the world and which he conscientiously answers.

### Heyrovsky the Man

In sacrifice to the major interest of his life, polarography, Professor Heyrovsky has given up most of his early interests. Once a pianist and a member of a student chamber music orchestra, he is today only a listener of music; he is fond of attending opera and still knows long parts of many by memory. At one time a well-known reviewer of books, today he hardly finds time to read novels, although when he wishes to brush up his knowledge of languages which is always admired by foreigners, he reads crime stories. He often repeats David Hume's critical comment that a book which does not contain any mathematical formulae is good only to be thrown into the fire.

Always interested in sports and once a mountaineer, soccer and tennis player, skier, and swimmer, Professor Heyrovsky has now, following the order of his

physician, limited himself to two short walks weekly. Nevertheless, he still makes a kick-off at the traditional soccer match between the Polarographic Institute and the Institute of Physical Chemistry. Every day he acknowledges his childhood love for animals and the outdoors by spending some time in the garden of the Institute (Fig. 5).

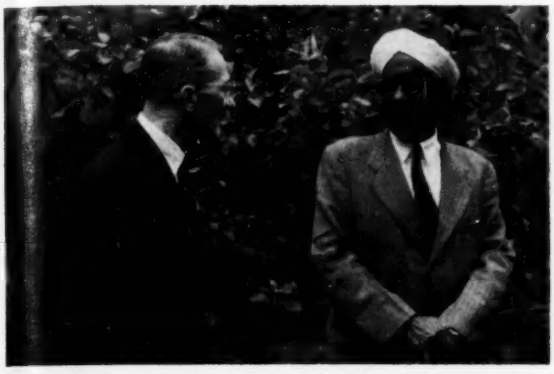

Figure 5. Sir C. Raman (Indian Nobel Prize winner) with Professor Heyrovsky in the garden of the Polarographic Institute, Prague.

Professor Heyrovsky is fond of guests, his hospitality having become proverbial. He likes good jokes, red wine, and good cooking, but dislikes smoking (the smokers in the Institute have to go out of the building to smoke; even then, they occasionally hear some sarcastic remarks). His pleasant sense of humor is most characteristically expressed during the annual Institute parties, where his speeches are spiced with good jokes; until a few years ago he and Professor Brdicka used to perform short improvised satirical plays based on scientific life. At these latter occasions, he showed his ability in make-up, usually involving long beards.

Mention has been made of Heyrovsky's son, Michael, who is now an active investigator in polarography.

Another member of Heyrovsky's family who steadily supported and encouraged Professor Heyrovsky during his whole scientific career is his devoted and charming wife, Marie, who, after serving for a long time as his unofficial secretary, became that officially in 1951. Their daughter Jitka (Czech for Judith) is a biochemist in a research institute.

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## Medicinal Chemistry Symposium Reprints Available

Reprints of the symposium "Fifty Years of Progress in Medicinal Chemistry," which appeared in the April 1960 issue of this Journal, are now available for $1.00 each, postpaid. The 34-page reprint contains "Volatile Anesthetics and Analgesics," by John C. Krantz, Jr; "The Chemotherapy of Infectious Disease, 1909–1959," by Jackson P. English; "Vitamins as Medicinal Agents," by Roger J. Williams; "Antihypertensive and Diuretic Agents; Past, Present, and Future," by Albert J. Plummer and Frederick F. Yonkman; "The Hormones," by Lewis H. Sarett; "The Role of the Biochemist in the Search for New Therapeutic Agents," by Sidney Udenfriend; "The Contributions of Medicinal Chemistry to Psychopharmacology," by C. Jelleff Carr; and "Impact of Research on the Growth of Medicinal Chemistry," by Max Tishler. Orders should be sent to:

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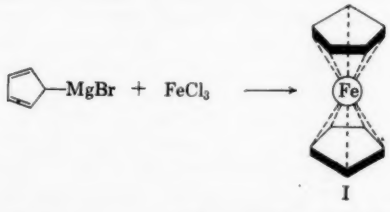
# Cyclopentadienyl Compounds of Metals and Metalloids

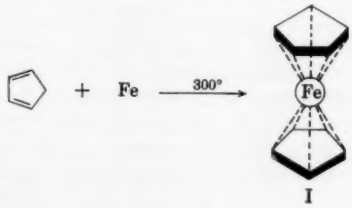
Organometallic chemistry has had a long and eventful history since its foundation in the 1840's by the famous researches of Bunsen on cacodyl and Frankland on organozinc compounds. In the ensuing century, the chemistry of organic compounds of metals and metalloids has played a significant role in developing our theories of valency and chemical bonding and has aided in a periodic classification of the elements. Organometallic compounds have proved to be valuable intermediates in the synthesis of other chemicals and have found direct commercial application in many instances. One need only mention Grignard's famous discovery of the formation and reactions of organomagnesium halides, Midgley's utilization of tetraethyllead as a gasoline antiknock agent, and Ziegler's recent remarkable discovery that ethylene can be polymerized by catalysts containing organoaluminum compounds in combination with metal salts as but a few of the examples that have greatly affected present-day chemistry and chemical technology.

In spite of the large amount of research in organometallic chemistry during the last century, however, it appeared that organic derivatives of the transition metals were generally inaccessible, although a few scattered claims concerning the synthesis of such derivatives had accumulated through the years (*1*). In 1951, two different groups, working independently, isolated an entirely new type of organometallic compound, biscyclopentadienyliron (I).[1] Kealy and Pauson isolated biscyclopentadienyliron from the reaction of cyclopentadienylmagnesium bromide and ferric chloride in diethyl ether solution (*2*).




I

Miller, Tebboth, and Tremaine obtained biscyclopentadienyliron from the reaction of cyclopentadiene vapor and reduced iron at 300° (*3*).




I

It is noteworthy that the isolation of biscyclopentadienyliron by both groups was completely unexpected.

Since the initial discovery of biscyclopentadienyliron, the chemistry of organic derivatives of the transition metals has expanded at an exceedingly rapid rate. A large portion of these investigations has been directed toward developing the chemistry of biscyclopentadienyliron itself. Shortly after the discovery of this new organo-iron compound, Woodward, Rosenblum, and Whiting found that it would undergo the Friedel-Crafts reaction and suggested the name *ferrocene* as a result of its aromatic reactivity (*4*). In recent years, numerous other chemical confirmations of the aromatic character of ferrocene have been reported (*5*). Biscyclopentadienylruthenium (*6*), biscyclopentadienylosmium (*6*), and cyclopentadienylmanganese tricarbonyl (*7*) likewise undergo substitution reactions that are characteristic of aromatic compounds, indicating that the scope of research in this area is much broader than the chemistry of ferrocene alone.

Another direction of research stimulated by the discovery of biscyclopentadienyliron has been the synthesis and structural elucidation of cyclopentadienyl derivatives of most of the other metals and metalloids, including many mixed cyclopentadienyl-metal carbonyls and nitrosyls. The purpose of the present review is to acquaint the reader with the versatile manner in which the cyclopentadienyl group can form organometallic and organometalloidal compounds with such a large number of the chemical elements. This review is not intended to be exhaustive, since the subject matter, even though resulting mostly from research since 1951, is entirely too abundant to be considered in detail in a review of this type. It is hoped that the review will stimulate the reader's interest in this series of chemical compounds, and that he will seek more detailed information concerning chemical and physical properties, structure, and bonding in either the original literature or in one of several recent comprehensive reviews which have appeared on this subject (*8*, *9*).

The cyclopentadienyl group forms compounds with more metals and metalloids than does any other organic group, including the more familiar ones such as methyl, ethyl, or phenyl. This widespread occurrence is well illustrated in Figure 1. The first cyclopentadienyl-metal compound was discovered by Thiele over 50 years ago (*10*), but it was the discovery of biscyclopentadienyliron in 1951 that stimulated the intensive interest in organometallic compounds of this type. A systematic approach will be followed in the present review in which various metals and metalloids within a

[1] In order to avoid ambiguity and confusion, the prefix "bis-" will be used throughout this review to designate two cyclopentadienyl groups attached to a metal or metalloid.

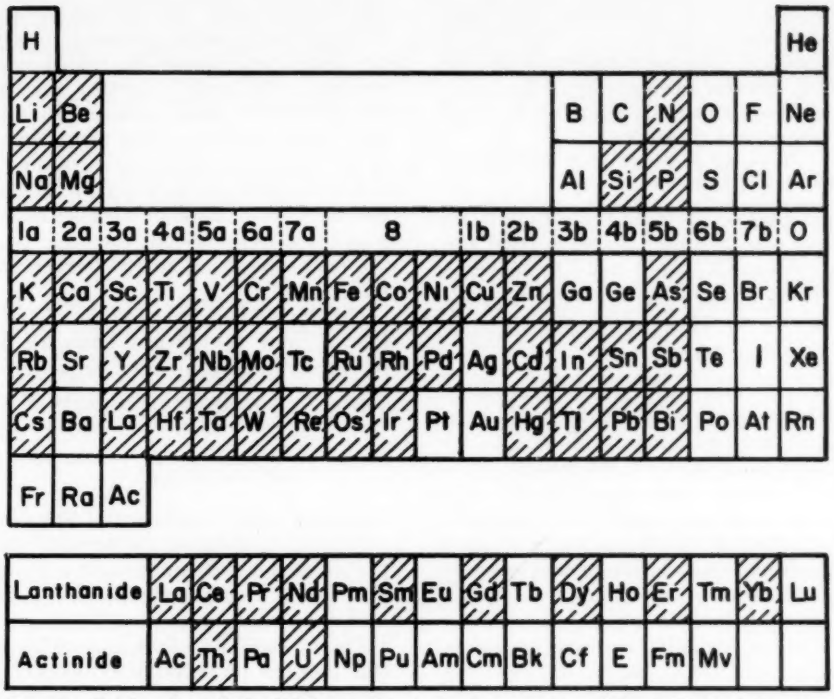

H
He
Li Be B C N O F Ne
Na Mg Al Si P S Cl Ar
Ia 2a 3a 4a 5a 6a 7a 8 Ib 2b 3b 4b 5b 6b 7b O
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn
Fr Ra Ac
Lanthanide La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Actinide Ac Th Pa U Np Pu Am Cm Bk Cf E Fm Mv

**Figure 1. Metals and metalloids which form cyclopentadienyl compounds are designated by shaded squares.**

given group of the periodic table will be briefly discussed in terms of the cyclopentadienyl compounds they can form.

### Bonding

The nature of the bonding between the metal or metalloid and the cyclopentadienyl ring can be rationalized by consideration of several extreme types. First, there can occur transfer of an electron from the metal to the cyclopentadienyl ring, resulting in a positively charged metal atom, a negatively charged cyclopentadienyl ring, and consequently an ionic bond. Cyclopentadienyl derivatives of sodium, potassium, and magnesium are examples of compounds possessing this type of bonding. Cyclopentadienyl-metal compounds in which the ring-to-metal bonding is essentially ionic are frequently referred to as "cyclopentadienides" in order to emphasize the anionic characteristics of the cyclopentadienyl ring.

Second, the metal or metalloid and *one* carbon atom of the cyclopentadienyl ring can each contribute an electron for bonding, resulting in a sharing of the pair of electrons. This type of bond formation represents a *localized* covalent bond, and can be referred to as a $\sigma$-bond. Cyclopentadienyl derivatives of silicon are good examples of compounds exhibiting this type of bonding.

A third extreme type of bonding can result in which the entire cyclopentadienyl ring is bonded uniformly to the metal atom. This type of bonding occurs principally in cyclopentadienyl compounds of the transition metals, such as biscyclopentadienyliron.[2] Bonding of this nature results from the overlap of $\pi$-electrons (viz., the electrons that are not involved in localized $\sigma$-bonding between the carbon atoms and between carbon and hydrogen atoms) of the cyclopentadienyl ring with the *d*-orbitals of the metal, and can therefore be referred to as $\pi$-bonding.

The extent of this overlap has been the subject of considerable dispute in recent years. Fischer and his school have interpreted the bonding in biscyclopentadienyliron, for example, to be similar to that found in the well-known penetration complexes such as the ion $[Fe(CN)_6]^{-4}$, in which the metal atom accepts three pair of $\pi$-electrons from each cyclopentadienyl ring into its vacant 3*d*, 4*s*, and 4*p* orbitals, with the attainment of an inert gas configuration (*8*). Others, on the basis of molecular orbital calculations, maintain that the chemical and physical properties of the transition metal-cyclopentadienyl compounds can best be explained by assuming a *delocalized* covalent bond between the metal atom and cyclopentadienyl ring as a whole (*9*).

It should be reiterated that the types of bonding described above represent limiting, extreme types. As in the case of many other chemical compounds, one can speak only of essentially ionic, essentially covalent, etc., bonding. The true state of affairs undoubtedly lies somewhere between these extremes.

### Related Organometallic Compounds

Before proceeding to a systematic discussion of the various types of compounds formed between metals or metalloids and the cyclopentadienyl group, it should be mentioned that other recent investigations have resulted in the synthesis of a vast number of structurally related organometallic compounds, such as bisbenzenechromium, thiophenechromium tricarbonyl, butadieneiron tricarbonyl, etc. The formation of organometallic

[2] Unless otherwise stated (e.g., biscyclopentadienylmanganese), this type of bonding occurs in all cyclopentadienyl-metal compounds of Groups IV-A, V-A, VI-A, VII-A, and VIII.

compounds by coordination of $\pi$-electrons of olefins and aromatics with transition metals, as exemplified by these compounds and by biscyclopentadienyliron, appears to be a fairly general phenomenon. The synthesis and study of these compounds is rapidly developing into a major new area of chemistry.

### Compounds of Group I-A Elements

Cyclopentadienyl compounds of all the alkali metals except francium are now known. Thiele isolated the first cyclopentadienyl-metal compound, cyclopentadienylpotassium, from the reaction of potassium and cyclopentadiene in benzene solution (*10*).

$$C_5H_6 + K \rightarrow C_5H_5K + {}^1/_2H_2$$

The reaction of cyclopentadiene with an alkali metal in a suitable solvent has become a very general procedure for the synthesis of the other cyclopentadienyl-alkali compounds. Solvents which have been used include tetrahydrofuran (*11–13*), liquid ammonia (*14, 15*), and xylene (*16, 17*). The yields in most cases are nearly quantitative. Cyclopentadienyllithium has also been obtained by reaction of cyclopentadiene and organolithium compounds, such as *n*-butyllithium and phenyllithium (*18, 19*).

All the cyclopentadienyl-alkali compounds are colorless when pure and rapidly decompose in air with coloration. They are insoluble in nonpolar solvents, exhibit varying degrees of solubility in solvents such as tetrahydrofuran, and are rapidly hydrolyzed by water. They react readily with carbon dioxide and alkyl halides (*16, 17*). The high solubility of the cyclopentadienyl-alkali compounds and the fact that they do not readily sublime except at very high temperatures had made them versatile intermediates in the synthesis of cyclopentadienyl derivatives of many other metals and metalloids.

The salt-like nature of the cyclopentadienyl-alkali compounds suggests that they are essentially ionic. It has been stated, for example, that the sodium-carbon bond in cyclopentadienylsodium is approximately 50 per cent ionic. The sodium cation is located above the negatively charged ring equidistant from all five carbon atoms in the crystal state (*16*). This point is illustrated by structure II.

II

### Compounds of Group II-A Elements

Cyclopentadienyl compounds of beryllium, magnesium, and calcium have been reported. Biscyclopentadienylberyllium has been recently prepared by the reaction of cyclopentadienylsodium and beryllium chloride, using diethyl ether as the reaction medium (*20*).

$$2C_5H_5Na + BeCl_2 \rightarrow (C_5H_5)_2Be + 2NaCl$$

Biscyclopentadienylberyllium is a diamagnetic, white crystalline solid. In many respects it exhibits properties that are characteristic of other organoberyllium compounds, since it is extremely sensitive to air and to moisture and is readily soluble in organic solvents that are free of oxygen. In contrast to many other organoberyllium compounds, however, biscyclopentadienylberyllium exists in monomeric form in solution and does not form an etherate. Further, the compound exhibits an appreciable dipole moment in solution excluding any symmetrical structural formulation. On the basis of these data and consideration of the infrared spectrum of biscyclopentadienylberyllium, it has been suggested that one cyclopentadienyl ring is bonded to beryllium by a localized $\sigma$-bond, while the other ring is $\pi$-bonded to the metal, resulting in $sp^3$ (tetrahedral) hybridization (*20*).

Cyclopentadienylmagnesium halides have been known since 1914, when Grignard and Courtot observed that methyl- or ethylmagnesium bromide reacted with acidic hydrocarbons such as cyclopentadiene, forming Grignard reagents (*21*).

$$RMgBr + C_5H_6 \rightarrow C_5H_5MgBr + RH$$
$$R = CH_3, C_2H_5$$

Cyclopentadienylmagnesium halides have proved to be valuable intermediates in the synthesis of other cyclopentadienyl-metal compounds although their use has now been largely superseded by cyclopentadienylsodium.

Biscyclopentadienylmagnesium has been prepared by the thermal decomposition of cyclopentadienylmagnesium bromide (*12, 22, 23*) and (more satisfactorily) by the direct reaction of cyclopentadiene vapor and magnesium metal (*24*).

$$2C_5H_6 + Mg \rightarrow (C_5H_5)_2Mg + H_2$$

The compound forms colorless crystals that rapidly decompose on exposure to air, moisture, and carbon dioxide. It is diamagnetic (*25*), but in contrast to biscyclopentadienylberyllium, it has essentially no dipole moment in solution (*20*). This fact suggests a symmetrical configuration, and biscyclopentadienylmagnesium has in fact been found to possess a "sandwich" structure in which the magnesium atom is centrally located between the two cyclopentadienyl rings (*26, 27*). The bonding in this compound is believed to be essentially ionic (*22, 28*).

Biscyclopentadienylcalcium has been reported to be formed from the reaction of cyclopentadiene and calcium carbide in a suitable solvent. It reacts readily with air and with carbon dioxide (*17, 29*).

### Compounds of Group III-A Elements

Triscyclopentadienyl compounds of scandium, yttrium, lanthanum, and many of the lanthanides have been prepared by the reaction of cyclopentadienylsodium with the metal chlorides in tetrahydrofuran (*30, 31*). These compounds are crystalline solids, unstable in air or in the presence of water, but possessing high thermal stabilities. The salt-like nature and magnetic properties indicate essentially ionic ring-to-metal bonding.

The possibility that analogous cyclopentadienyl derivatives of some of the actinides could be isolated has been investigated by Reynolds and Wilkinson (*32*). They found that the reaction between cyclopentadienylsodium and uranium tetrachloride produced a dark-red crystalline compound of the formula $C_{15}H_5UCl$ in almost quantitative yield. This compound, which

has been formulated as triscyclopentadienyluranium chloride, is readily oxidized by air and forms green aqueous solutions containing the cation $[U(C_5H_5)_3]^+$. It has been proposed that all three cyclopentadienyl rings are $\pi$-bonded to the uranium atom in a symmetrical manner.

Cyclopentadienylthorium compounds have likewise been isolated, but the yields of these compounds are so low that they are not yet well characterized (*32*).

### Compounds of Group IV-A Elements

Probably the best known cyclopentadienyl compound of the metals in this group is biscyclopentadienyltitanium dichloride. It can be readily prepared in the form of deep-red crystals by the reaction of titanium tetrachloride and cyclopentadienylsodium in tetrahydrofuran solution (*33*).

$$TiCl_4 + 2C_5H_5Na \rightarrow (C_5H_5)_2TiCl_2 + 2NaCl$$

Cyclopentadienylmagnesium bromide and titanium tetrachloride yield biscyclopentadienyltitanium dibromide (*33*, *34*). Corresponding iodides, fluorides, hydroxyfluorides, etc., are also known. These compounds are stable in air and are diamagnetic.

The biscyclopentadienyltitanium dihalides have been used in the synthesis of other novel organotitanium derivatives. The reaction of biscyclopentadienyltitanium dichloride and lithium aryls has produced a number of diaryl-biscyclopentadienyltitanium compounds (*35*, *36*). Some of these compounds exhibit fair stability at room temperature although dimethylbiscyclopentadienyltitanium is reported to be thermally very unstable (*37*). The reaction of biscyclopentadienyltitanium dichloride with either cyclopentadienylsodium or butyllithium followed by treatment of the intermediate products with carbon monoxide under pressure has resulted in the formation of the first carbonyl derivative of titanium, biscyclopentadienyltitanium dicarbonyl (*38*). Complexes formed from the reaction of biscyclopentadienyltitanium dichloride and alkyl-aluminum compounds have been found to exhibit varying degrees of catalytic activity in the low pressure polymerization of ethylene (*39–42*). Reduction of biscyclopentadienyltitanium dichloride with zinc dust yields the green crystalline compound $(C_5H_5)_2TiCl$ (*43*).

Cyclopentadienyltitanium trichloride has been reported by several groups of investigators. This compound can be obtained by a redistribution reaction between titanium tetrachloride and biscyclopentadienyltitanium dichloride (*44*), by cleavage of the latter compound with chlorine (*44*), and by reaction of biscyclopentadienylmagnesium and titanium tetrachloride (*45*). Corresponding tribromides and triiodides have also been prepared (*45*).

Biscyclopentadienyltitanium, in which the metal can be considered to be divalent, has been obtained by the reaction of titanium dichloride and cyclopentadienylsodium (*46*). In contrast to many of the tetravalent cyclopentadienyl-titanium compounds, biscyclopentadienyltitanium is exceedingly sensitive to air.

Biscyclopentadienylzirconium dibromide has been obtained as nearly colorless crystals from the reaction of cyclopentadienylmagnesium bromide and zirconium tetrabromide (*33*, *34*). It is less soluble in organic solvents, more readily soluble in water, and less readily hydrolyzed than its titanium analogue. Biscyclopentadienylhafnium dichloride has been mentioned in the patent literature (*47*).

### Compounds of Group V-A Elements

Biscyclopentadienyl metal halides of vanadium, niobium, and tantalum have been reported by reaction of the appropriate metal halide with either cyclopentadienylsodium or cyclopentadienylmagnesium halides (*33*, *34*). An example is the synthesis of biscyclopentadienylvanadium dichloride.

$$VCl_4 + 2C_5H_5Na \rightarrow (C_5H_5)_2VCl_2 + 2NaCl$$

Starting with niobium or tantalum pentabromides, the pentavalent biscyclopentadienylniobium and biscyclopentadienyltantalum tribromides have been made (*34*). Biscyclopentadienylvanadium dichloride is a pale-green, paramagnetic substance and is partly soluble in most organic solvents. Reduction of aqueous solutions of this compound with amalgamated zinc (Jones reductor) yields the $[(C_5H_5)_2V]^+$ cation (*34*).

A cyclopentadienyl derivative of divalent vanadium, biscyclopentadienylvanadium, has been obtained from the reaction of excess cyclopentadienylmagnesium bromide and vanadium tetrachloride (*48*, *49*), by reaction of cyclopentadienylsodium and vanadium trichloride (*22*), and by reduction of biscyclopentadienyl vanadium dichloride with lithium aluminum hydride (*43*). The purple-black, paramagnetic compound is soluble in common organic solvents and is stable only in the absence of air. A "sandwich" structure has been proposed as the result of X-ray studies (*26*, *27*).

Biscyclopentadienylvanadium chloride has been isolated from the reaction of biscyclopentadienylvanadium dichloride and two equivalents of phenyllithium followed by treatment with hydrogen chloride and also by mixing equivalent amounts of biscyclopentadienylvanadium dichloride and biscyclopentadienylvanadium in organic solvents (*50*). From reaction of biscyclopentadienylvanadium chloride and an equivalent amount of phenyllithium, black air-sensitive crystals of phenyl-biscyclopentadienylvanadium have been isolated. It is postulated that in this compound, as in the aryl derivatives of biscyclopentadienyltitanium, the cyclopentadienyl groups are $\pi$-bonded and the phenyl group is $\sigma$-bonded to the metal (*50*).

The first reported carbonyl compound of vanadium, cyclopentadienylvanadium tetracarbonyl, has been obtained from the reaction of biscyclopentadienylvanadium and carbon monoxide at elevated temperatures and under pressure (*48*, *49*).[3] This bright-orange compound is diamagnetic and is stable in air for short periods of time. In the presence of a mixture of hydrogen chloride and oxygen it is converted to cyclopentadienyloxychloride (*51*).

$$C_5H_5V(CO)_4 + 2HCl + O_2 \rightarrow C_5H_5VOCl_2 + 4CO + H_2O$$

Cyclopentadienylvanadium tetracarbonyl can be

[3] A pure vanadium carbonyl, divanadium dodecacarbonyl, is also now known (PRUETT, R. L., AND WYMAN, J. E., *Chem. & Ind.*, 119 (1960).

reduced with sodium in liquid ammonia to a yellow sodium salt in which the vanadium is uninegative (*49*).

$$C_5H_5V(CO)_4 + 2\ Na \rightarrow Na_2[C_5H_5V(CO)_3] + CO$$

### Compounds of Group VI-A Elements

Biscyclopentadienylchromium has been prepared by a variety of methods, including the reaction of either cyclopentadienylsodium (*22*, *52*) or cyclopentadienylmagnesium bromide (*48*, *53*) and chromium trichloride in an ethereal solvent, and by a vapor phase reaction of chromium hexacarbonyl and cyclopentadiene (*54*). The scarlet, paramagnetic compound is extremely sensitive to air. A "sandwich" structure has been proposed as the result of X-ray studies (*55*).

In view of the well-known ability of Group VI-A metals to form carbonyls, a detailed investigation has been made of the possible reaction of biscyclopentadienylchromium and carbon monoxide under pressure and at various temperatures (*56*). At 100–10° and 100 atmospheres pressure, a brown-black, salt-like product was obtained and formulated as $[Cr(C_5H_5)_2]^+[C_5H_5Cr(CO)_3]^-$. At 150–70°, blue-green, diamagnetic biscyclopentadienyl-dichromium hexacarbonyl, $[C_5H_5Cr(CO)_3]_2$, was the principal product.[4] If hydrogen is present in the above carbonylation reaction, yellow, diamagnetic, air-sensitive cyclopentadienylchromium tricarbonyl hydride can be formed (*53*, *56*). The hydrogen atom is weakly acidic, and the compound dissolves in aqueous alkali.

$$C_5H_5Cr(CO)_3H + NaOH \rightarrow Na[C_5H_5Cr(CO)_3] + H_2O$$

The resulting air-stable anion can be precipitated by cations such as the mercuric ion.

Biscyclopentadienylmolybdenum chloride has been isolated in the form of green diamagnetic crystals from the reaction of cyclopentadienylsodium and molybdenum pentachloride. From cyclopentadienylmagnesium bromide and molybdenum pentachloride, cations of the type $[(C_5H_5)_2MoCl]^+$ and $[(C_5H_5)_2MoCl_2]^+$ have been obtained; these cations can be precipitated from aqueous solution with heavy metal anions. Tungsten hexachloride reacts similarly to form the cation $[(C_5H_5)WCl_2]^+$ (*52*).

In a manner analogous to the preparation of the chromium compound, biscyclopentadienyl-dimetal hexacarbonyls of both molybdenum and tungsten have been obtained (*52*, *54*). An X-ray study of the molybdenum compound indicates a non-linear molecular arrangment with a metal-metal bond and non-bridging carbonyl groups (*57*, *58*). Cyclopentadienyl-metal tricarbonyl hydrides of both molybdenum and tungsten have also been made and together with the chromium analogue have been used in the synthesis of novel cyclopentadienyl-metal carbonyl derivatives that contain $\sigma$-bonded alkyl or aryl groups as well. Cyclopentadienyl-nitrosyl compounds of the Group VI-A metals have also been extensively studied (*8*, *9*).

Several other mixed cyclopentadienyl compounds of chromium deserve special mention. The reaction of equivalent amounts of cyclopentadienylmagnesium bromide and chromium (III) acetylacetonate has produced cyclopentadienylchromium acetylacetonate bromide, in which the chromium atom is $\pi$-bonded to the cyclopentadienyl group and is also part of a chelate ring (*59*). Cyclopentadienylbenzene-chromium, in which both the cyclopentadienyl ring and the benzene ring are $\pi$-bonded to the metal, has been isolated from the reaction of phenylmagnesium bromide, cyclopentadienylmagnesium bromide, and chromium trichloride, followed by hydrolysis (*60*).

### Compounds of Group VII-A Elements

Biscyclopentadienylmanganese has been prepared by the reaction of manganous halides and either cyclopentadienylsodium (*12*, *22*) or cyclopentadienylmagnesium bromide (*61*). This compound forms air-sensitive crystals that are amber-brown at room temperature. Upon heating, a transition to a light-pink modification occurs at 159°; the melting point is 173°. The transition is reversible on slow cooling. The chemical and magnetic properties of biscyclopentadienylmanganese indicate that the compound is essentially ionic. This conclusion receives strong support from infrared and mass spectra studies (*22*). The ionic nature of biscyclopentadienylmanganese is in contrast to the principally $\pi$-bonded derivatives of the other metals in the first transition series and undoubtedly results from the extra stability attained by the half-filled 3*d* shell of the manganous ion.

The reaction product of cyclopentadienylsodium and manganous bromide, or biscyclopentadienylmanganese itself, can react with carbon monoxide at elevated temperatures under pressure to yield cyclopentadienylmanganese tricarbonyl (*61*, *62*). This compound exists in the form of pale-yellow, diamagnetic crystals and, in contrast to biscyclopentadienylmanganese, is stable in the air. The cyclopentadienyl ring is $\pi$-bonded to the metal, and the compound has been found to undergo typical aromatic-type substitution reactions (*7*).

The reaction of cyclopentadienylsodium and rhenium pentachloride in tetrahydrofuran solution is unique in that a hydride, biscyclopentadienylrhenium hydride, is the only organo-rhenium compound formed (*63*). The preparation of this compound has recently been improved by treatment of the reaction mixture with sodium borohydride (*64*). The hydrogen atom is not acidic as in other metal-carbonyl hydrides, but to the contrary, the compound behaves as a base and dissolves in hydrochloric acid to form a complex cation.

$$(C_5H_5)_2ReH \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} [(C_5H_5)_2ReH_2]^+$$

Biscyclopentadienylrhenium hydride is diamagnetic. High resolution nuclear magnetic resonance studies indicate that the hydrogen atom is highly shielded (*63*, *64*).

Biscyclopentadienylrhenium hydride has been found to react with carbon monoxide under pressure, forming a compound described as $(C_5H_5)_2ReH(CO)_2$ (*65*). This compound is stable in the air, diamagnetic, and has neither acidic or basic properties. In the original formulation, it was suggested that one cyclopentadienyl ring was bonded to rhenium by a localized $\sigma$-bond, while the remaining cyclopentadienyl ring and hydrogen atom were bound as in biscyclopentadienylrhenium

[4] Cotton and Wilkinson (*52*,*54*) first obtained mixed carbonyls of this type from cyclopentadiene and metal hexacarbonyls. The chromium and molybdenum derivatives were originally formulated incorrectly.

hydride (*65*). Later studies have questioned the correctness of this formulation, and the proposal has been made that the compound is not a hydride, but instead π-cyclopentadienyl-cyclopentadiene-rhenium dicarbonyl, $C_5H_5Re(C_5H_6)(CO)_2$ (*66*).

From the reaction of rhenium pentachloride and cyclopentadienylsodium followed by treatment of the product with carbon monoxide at high temperatures and under pressure, cyclopentadienylrhenium tricarbonyl has been isolated as an air-stable, yellow product (*67*). This compound has also been obtained directly from rhenium carbonyl and dicyclopentadiene (the dimer of cyclopentadiene) (*66*).

### Compounds of Group VIII Elements

*Iron, ruthenium, osmium.* Certainly the best known cyclopentadienyl compound of all the metals and metalloids is biscyclopentadienyliron, or ferrocene. The chemical and physical properties of this remarkable organometallic compound have been extensively studied, and only a short synopsis can be given in this review. Since the two original syntheses of ferrocene (*2, 3*), a number of improved procedures for its preparation have become available. Ferrocene now can be best produced either by the reaction of anhydrous ferrous chloride and cyclopentadienylsodium in tetrahydrofuran solution, or by the reaction of iron halides and cyclopentadiene in diethylamine (*68*).

$$2C_5H_5Na + FeCl_2 \rightarrow (C_5H_5)_2Fe + 2NaCl$$

$$2C_5H_6 + FeCl_2 + 2(C_2H_5)_2NH \rightarrow (C_5H_5)_2Fe + 2(C_2H_5)_2NH\cdot HC$$

Ferrocene forms air-stable, orange crystals, mp 174°. It is soluble in common organic solvents and is insoluble in and unattacked by water, sodium hydroxide solution, and even concentrated hydrochloric acid at the boiling point (*2*). Ferrocene has been found to be diamagnetic and appears to be thermally stable to at least 470°. It can be oxidized in solution to a blue, water soluble cation, $[Fe(C_5H_5)_2]^+$ (*69*). Reactions of ferrocene with maleic anhydride or with hydrogen under the usual conditions have not been successful, indicating that a conjugated diene system as in cyclopentadiene no longer exists (*4*). The extensive chemistry of aromatic substitution reactions of ferrocene has been reviewed previously (*5*). Both physical and chemical evidence indicate that the cyclopentadienyl rings in ferrocene are freely rotating in solution and in the vapor phase.

Consideration of these properties and a preliminary X-ray study of ferrocene has led to the postulation of a centrosymmetric structure (I), in which the iron atom is "sandwiched" between the two cyclopentadienyl rings (*69, 70*). A Fourier analysis has confirmed the "sandwich" structure and has shown that the carbon atoms of the two cyclopentadienyl rings are staggered with respect to each other (*71*). Thermodynamic properties, infrared and Raman spectra, and other physical properties of ferrocene have likewise been extensively studied (*8, 9*).

A ruthenium analogue of ferrocene, biscyclopentadienylruthenium, was first prepared by the reaction of ruthenium (III) acetylacetonate and cyclopentadienylmagnesium bromide (*72*). More recently, the reaction of cyclopentadienylsodium and ruthenium trichloride or osmium tetrachloride has led to the synthesis of biscyclopentadienylruthenium and biscyclopentadienylosmium, respectively (*6, 73*). Both compounds are air-stable, the ruthenium analogue forming light yellow crystals and the osmium compound forming white crystals. Like ferrocene, both biscyclopentadienylruthenium and -osmium can be oxidized to higher valent cations, but with increasing difficulty (*73*). Both compounds have been found to undergo aromatic substitution reactions in varying degrees (*6*). X-ray crystallographic studies have shown that both biscyclopentadienylruthenium and -osmium have "sandwich" structures, but compared to ferrocene, the carbon atoms of one cyclopentadienyl ring eclipse those of the other ring in the form of a prism (*74, 75*). This configuration is illustrated by structure III.

III

The reaction of iron pentacarbonyl and dicyclopentadiene has produced another cyclopentadienyliron derivative, biscyclopentadienyl-diiron tetracarbonyl $[(C_5H_5)_2Fe(CO)_2]_2$ (*52, 62, 76, 77*).[5] It is a dark purple, diamagnetic, air-stable solid. A detailed X-ray study of this compound indicates an iron-iron bond and both bridging and non-bridging carbonyl groups (*78*).

The reactions of biscyclopentadienyl-diiron tetracarbonyl are also of interest. Reduction of this compound with sodium amalgam produces the anion $[C_5H_5Fe(CO)_2]^-$ (*76*). Oxidation of solutions of biscyclopentadienyl-diiron tetracarbonyl in the presence of hydrogen halides or halogens has yielded cyclopentadienyliron dicarbonyl halides (*37, 62, 77, 79, 80*). By the reaction of the sodium salt of the anion $[C_5H_5Fe(CO)_2]^-$ with alkyl or aryl halides, and by reaction of cyclopentadienyliron dicarbonyl halides with Grignard reagents, organosodium or organolithium compounds, a variety of σ-bonded alkyl and aryl cyclopentadienyliron dicarbonyl derivatives have been obtained (*79, 80*). A similar compound containing an iron-silicon σ-bond has recently been made (*81*).

$$Na[C_5H_5Fe(CO)_2] + (CH_3)_3SiCl \rightarrow C_5H_5(CO)_2FeSi(CH_3)_3 + NaCl$$

*Cobalt, rhodium, iridium.* The first attempts to cause reaction of cyclopentadienylmagnesium bromide with either cobalt (III) acetylacetonate or cobaltous bromide resulted in formation of the very stable cation $[(C_5H_5)_2Co]^+$ (*82, 83*). This cation is isoelectronic with ferrocene and is therefore diamagnetic. A variety of salts have been formed, especially with heavy metal anions.

The neutral compound biscyclopentadienylcobalt has been more recently prepared by the action of cyclopentadienyl-alkali compounds on the complex $[Co(NH_3)_6](SCN)_2$ in liquid ammonia (*84*), by reduction of the $[Co(C_5H_5)_2]^+$ ion with lithium aluminum hydride

[5] This compound was erroneously formulated as $(C_5H_5)_2Fe_2(CO)_5$ in *52*.

(*43*), or most conveniently by the direct reaction of cyclopentadienylsodium and cobaltous or cobaltic chlorides (*22*). In contrast to the cation, biscyclopentadienylcobalt is paramagnetic and is extremely sensitive to oxidation.

The cations $[Rh(C_5H_5)_2]^+$ and $[Ir(C_5H_5)_2]^+$ can be obtained from the reaction of cyclopentadienylmagnesium bromide and either rhodium (III) acetylacetonate or iridium (III) acetylacetonate (*85*). They are very stable, in analogy with the $[Co(C_5H_5)_2]^+$ cation.

Several cyclopentadienyl compounds of nickel, rhodium, and iridium have been recently reported in which other ligands are present. Cyclopentadienyl-cyclopentadiene-metal derivatives have been obtained by reduction of the $[Co(C_5H_5)_2]^+$ and $[Rh(C_5H_5)_2]^+$ cations with sodium borohydride (*86*), and by reaction of rhodium or iridium trichlorides with cyclopentadienylpotassium and cyclopentadiene (*87*). In these compounds, the cyclopentadienyl ring is assumed to be $\pi$-bonded to the metal atom, while the cyclopentadiene ring contributes two pair of $\pi$-electrons. Cyclopentadienylcobalt dicarbonyl, a dark-red, diamagnetic liquid, has been prepared by the reaction of biscyclopentadienylcobalt and carbon monoxide at elevated temperatures under pressure (*88*) and by the reaction of dicobalt octacarbonyl and cyclopentadiene at room temperature (*62*). A mixed cyclopentadienylrhodium complex of cycloocta-1,5-diene is also known (*89*).

*Nickel, palladium, platinum.* Biscyclopentadienylnickel has been prepared from the reaction of cyclopentadienylmagnesium bromide and nickel (II) acetylacetonate (*33, 90*) and by the reaction of cyclopentadienylpotassium and the complex $[Ni(NH_3)_6]$ $(SCN)_2$ (*90*). It forms green paramagnetic crystals that are moderately stable in air. Oxidation produces the cation $[(C_5H_5)_2Ni]^+$. Attempts to carry out aromatic-type substitution reactions on biscyclopentadienylnickel have thus far been unsuccessful. Mixed cyclopentadienylnickel derivatives containing carbonyl and nitrosyl ligands have also been obtained from the reaction of biscyclopentadienylnickel and nickel tetracarbonyl or nitric oxide (*62, 91, 92*).

The reaction of an aqueous solution of palladium dichloride and cyclopentadiene has produced a dark brown material believed to be cyclopentadienylpalladium chloride. The material is probably polymeric with chloro-bridges (*93*).

Potassium chloroplatinite and dicyclopentadiene react to form a stable complex, but physical evidence indicates that it is not a cyclopentadienylplatinum derivative (*94*).

### Compounds of Group I-B Elements

Attempts to synthesize copper (I) or copper (II) cyclopentadienyls by reaction of copper halides with cyclopentadienyl-metal compounds have not been successful. Nevertheless, a rather unusual derivative, cyclopentadienyl-triethylphosphine-copper (I), has been prepared by the reaction of cyclopentadiene and triethylphosphine with copper (I) oxide (*95*). The compound exists as white crystals that are very slowly oxidized in air. It is insoluble in and unattacked by water and is readily soluble in common organic solvents. The ring-to-copper bonding in cyclopentadienyl-triethylphosphine-copper(I) is believed to be of the localized $\sigma$-type (*95*).

No cyclopentadienyl compounds of silver or gold have been reported.

### Compounds of Group II-B Elements

The reaction of cyclopentadienylsodium and zinc chloride in diethyl ether has produced biscyclopentadienylzinc in low yield (*96*). This colorless, diamagnetic, air-sensitive compound partly decomposes when sublimed at elevated temperatures. It is rapidly hydrolyzed in aqueous solution and is practically insoluble in many organic solvents. The salt-like nature of biscyclopentadienylzinc and the similarity of its infrared spectrum to that of biscyclopentadienylmagnesium suggest a "sandwich" structure as in the magnesium compound (*96*).

The less stable cadmium derivative decomposes with separation of cadmium under the reaction conditions employed for biscyclopentadienylzinc (*8*).

Biscyclopentadienylmercury has been prepared by the reaction of cyclopentadienylsodium and mercuric chloride in tetrahydrofuran (*95*). The pale yellow crystalline compound is stable in the presence of water, but is readily decomposed by light or heat. Biscyclopentadienylmercury is soluble in most organic solvents and forms a Diels-Alder adduct in benzene solution. The chemical and physical properties of this compound indicate a localized $\sigma$-bond between the cyclopentadienyl groups and mercury (*95*).

### Compounds of Group III-B Elements

No cyclopentadienyl derivatives of boron, aluminum, or gallium have yet been reported.

Both cyclopentadienylindium and triscyclopentadienylindium have been isolated from the reaction of cyclopentadienylsodium and indium(III) chloride in ethereal solvents (*97*). Triscyclopentadienylindium was isolated in very small amounts and was possibly an intermediate in the formation of cyclopentadienylindium, since it was converted to the latter compound during sublimation. The pale yellow, crystalline cyclopentadienylindium is extremely sensitive to air. It represents the first organometallic compound of indium (I) ever prepared. It is postulated that the remarkable stabilization of the monovalent derivative is due to coordination of three pair of $\pi$-electrons of the cyclopentadienyl anion with the three vacant $5p$ orbitals of the centrally located indium (I) cation, resulting in xenon configuration (*97*).

The reaction of cyclopentadiene with thallium hydroxide or thallium salts in the presence of alkali in aqueous solution has produced cyclopentadienylthallium in good yield (*98, 99*).

$$C_5H_6 + TlOH \xrightarrow{OH^-} C_5H_5Tl + H_2O$$

This reaction appears to be specific for the synthesis of cyclopentadienyl derivatives of thallium and has been suggested as an analytical method for thallous ion (*99*). Cyclopentadienylthallium is a pale yellow diamagnetic compound and is fairly stable in the air. It is practically insoluble in water and only slightly soluble in common organic solvents.

The relatively high stability of cyclopentadienylthallium is unusual since no other alkyl or aryl derivatives of thallium (I) have been isolated. The nature of the bonding is still in dispute. Both bonding analogous to that occurring in cyclopentadienylindium (*98*) and ionic bonding (*28*) have been proposed. Cyclopentadienylthallium has also been obtained from the direct reaction of cyclopentadiene vapor and thallium metal at elevated temperatures (*20*).

### Compounds of Group IV-B Elements

Tetravalent compounds of silicon and tin and divalent compounds of tin and lead are known. No cyclopentadienyl derivatives of germanium have yet been reported.

Cyclopentadienylsilanes have been prepared by the reaction of cyclopentadienyl-metal compounds with various chlorosilanes. The reaction of cyclopentadienylsodium with an excess of silicon tetrachloride has produced cyclopentadienyltrichlorosilane (*16*).

$$C_5H_5Na + SiCl_4 \rightarrow C_5H_5SiCl_3 + NaCl$$

Cyclopentadienylmethylsilanes have been prepared by the reactions of cyclopentadienylmagnesium bromide and methylchlorosilanes (*100*). Reaction of cyclopentadienyllithium with a twofold excess of dimethyldichlorosilane has been used to obtain cyclopentadienyldimethylchlorosilane (*101*). All the cyclopentadienylsilanes mentioned are liquids at room temperature and darken on standing in air. They readily undergo the Diels-Alder reaction with maleic anhydride to yield isolable, stable adducts. The diene character remains intact, as in cyclopentadiene, and indicates a localized covalent, $\sigma$-bond between the cyclopentadienyl ring and silicon.

The reaction of cyclopentadienylmagnesium bromide and various phenyltin chlorides has produced a series of cyclopentadienylphenyltin derivatives (*102*). A tetrasubstituted cyclopentadienyl derivative of tin was likewise obtained from cyclopentadienylmagnesium bromide and tin (IV) chloride although it was found to be pyrophoric and was not isolated in the pure state (*102*).

The freshly prepared cyclopentadienyl compounds of tin (IV) are light yellow in color. They darken slowly on standing although the rate of apparent decomposition is rapidly accelerated by both air and light. The cyclopentadienyl group in triphenylcyclopentadienyltin is readily cleaved by water, bromine, or *n*-butyllithium. It has been suggested that these organotin compounds resemble the salt-like cyclopentadienyl-alkali compounds. On the other hand, bands characteristic of conjugated double bonds are present in the infrared spectra of cyclopentadienyltin derivatives, and triphenylcyclopentadienyltin readily reacts with a number of dieneophiles to form stable adducts. These facts would indicate normal covalent bonding between the cyclopentadienyl ring and the tin atom.

Biscyclopentadienyltin has been readily obtained from the reaction of tin (II) chloride and cyclopentadienyllithium in dimethylformamide solution (*103*), whereas virtually all other organometallic derivatives of tin (II) exists as complex, probably polymeric compounds.

$$2C_5H_5Li + SnCl_2 \rightarrow (C_5H_5)_2Sn + 2LiCl$$

An alternate synthesis of biscyclopentadienyltin consists of the reaction of tin (II) chloride and cyclopentadienylsodium in refluxing ammonia (*104*).

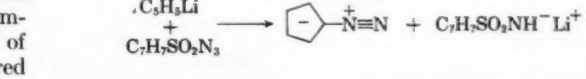
Biscyclopentadienyltin is isolated in the form of colorless, air-sensitive crystals. It does not hydrolyze in cold water but is readily cleaved by acids to yield cyclopentadiene. Biscyclopentadienyltin is diamagnetic and exhibits a dipole moment of 1.01 Debye in benzene solution; it is monomeric in benzene. Normal covalent bonding was originally proposed for this compound (*103*). Recent observations of the very striking similarity of the infrared spectrum of biscyclopentadienyltin to the spectra of cyclopentadienyl derivatives of the transition metals, as well as consideration of the nuclear magnetic resonance spectrum, now indicate that the compound has a partial "sandwich" configuration in which the rings are slightly inclined toward each other (*104–06*).

Biscyclopentadienyllead has been prepared by the reaction of cyclopentadienylsodium and lead nitrate in dimethylformamide solution (*107*), and by the reaction of cyclopentadienylsodium and lead (II) chloride in refluxing ammonia (*104*). The compound is very sensitive to oxidation; it is not soluble in water and does not react with it. Biscyclopentadienyllead is diamagnetic and has a pronounced dipole moment of 1.63 Debye in benzene. The structure and bonding of this compound are similar to that described for biscyclopentadienyltin (*104–06*).

### Compounds of Group V-A Elements

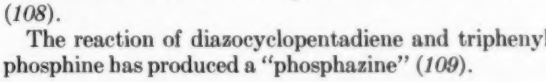
Nitrogen and phosphorus are certainly not metallic, and it is questionable to classify these elements as metalloids. Nevertheless, the compounds formed between the cyclopentadienyl group and nitrogen and phosphorus are of significant interest and are therefore included in this review. Cyclopentadienyl derivatives of both nitrogen and phosphorus are known in which the ring may be considered to possess six $\pi$-electrons, resulting in an effective negative charge on the cyclopentadienyl ring. The stability of these compounds can be regarded to result from resonance contributions of this type. As a result, such compounds are usually referred to as "cyclopentadienylides."

In 1953, Doering and DePuy reported the successful synthesis of diazocyclopentadiene from the reaction of cyclopentadienyllithium and *p*-toluenesulfonyl azide (*19*).



Diazocyclopentadiene is a reactive red liquid. It has been utilized in the synthesis of azoferrocenes (*108*).

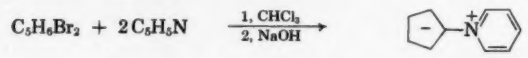
The reaction of diazocyclopentadiene and triphenylphosphine has produced a "phosphazine" (*109*).



This phosphazine fails to undergo thermal loss of nitrogen as do other phosphazines.

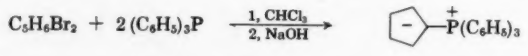
A somewhat different approach to the synthesis of cyclopentadienyl derivatives of nitrogen has recently

been described. When one equivalent of dibromocyclopentene was reacted with two equivalents of pyridine in chloroform solution and the resulting mixture was treated with alkali, a red-brown crystalline solid was isolated which has been formulated as pyridinium cyclopentadienylide (*110–12*).



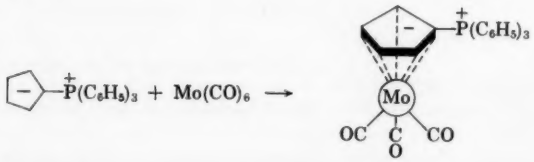
The compound slowly oxidizes in air, especially if exposed to light; it does not melt below 350°. Pyridinium cyclopentadienylide is only partly soluble in most organic solvents. Its solutions, however, are intensely colored, varying with the degree of polarity of the solvent. The structure of the compound was confirmed by catalytic hydrogenation to N-cyclopentylpiperidine.

Another interesting "ylide," triphenylphosphoniumcyclopentadienylide, has recently been prepared from the reaction of dibromocyclopentene with two equivalents of triphenylphosphine, followed by treatment with alkali (*113*).



This compound is not affected by aqueous or alcoholic potassium hydroxide solution and does not react with ketones as do many related phosphine-methylenes. As in the case of the cyclopentadienyl-nitrogen compounds, the remarkable stability of the phosphorus derivative results from contributions in which the cyclopentadienyl ring can be considered to possess an effective negative charge. Such a formulation of triphenylphosphoniumcyclopentadienylide would indicate that stabilization of the six $\pi$-electrons in the cyclopentadienyl ring might result in aromaticity of the ring. This appears to be the case, in view of the facile coupling reaction of this compound with aryldiazonium salts (*114*).

Abel, Singh, and Wilkinson have reasoned that the cyclopentadienyl ring in triphenylphosphoniumcyclopentadienylide might function as a formal six $\pi$-electron donor and replace carbon monoxide in metal carbonyls. Experimentally, these workers have found that this phosphorus "ylide" and molybdenum hexacarbonyl react readily in refluxing ethylene glycol dimethyl ether to yield triphenylphosphoniumcyclopentadienylide-molybdenum tricarbonyl in good yield (*115*).



Chromium and tungsten hexacarbonyls are reported to form similar metal derivatives.

Triscyclopentadienylbismuth has been prepared by the reaction of cyclopentadienylsodium and bismuth trichloride (*116*). The compound is very sensitive to oxidation. It exists in the form of orange-red crystals at low temperatures. On heating to about 20°, however, transformation occurs readily and irreversibly to a black polymeric form. Both forms are diamagnetic and can be hydrolyzed to yield cyclopentadiene.

Related experiments indicate that triscyclopentadienylantimony can be obtained by carrying out the reaction at low temperatures. An arsenic derivative has also been isolated, but it appears to be polymeric in nature (*116*)[6].

## Compounds of Group VI-B and Group VII-B Elements

In Groups VI-B and VII-B, only selenium, tellurium, polonium, iodine, and probably astatine can be considered to possess metalloidal properties. The organometallic chemistry of polonium and astatine is practically unknown, however, and while many selenides and tellurides have been prepared, no cyclopentadienyl derivatives of selenium or tellurium have been reported.

The reaction of cyclopentadienylmagnesium bromide and iodine in toluene solution resulted in the formation of a black, non-crystalline, insoluble powder. The product is believed to be a polymer (*117, 118*).

## Substituted Cyclopentadienyl Compounds

While cyclopentadienyl derivatives of metals and metalloids have been of great interest in recent years, a variety of similar compounds involving substituted cyclopentadienyl groups have also been prepared. Substituted cyclopentadienes such as methylcyclopentadiene, phenylcyclopentadiene, indene, and fluorene, as well as others of more complex nature, form organometallic or organometalloidal compounds by replacement of a hydrogen atom. A detailed discussion of these compounds is beyond the scope of this review.

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[6] Note added in proof: Details of the synthesis and properties of cyclopentadienylbismuth and -antimony compounds are now available. See Fischer, E. O., and Schreiner, S., *Chem. Ber.*, **93**, 1417 (1950).

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# The Heat of Mixing of Organic Liquids

A calorimetric experiment on the heat of mixing of organic liquids may be performed in the undergraduate physical chemistry laboratory either as an alternate for or as a supplement to the standard heat of ionic reactions experiment where a Dewar flask is used as an adiabatic calorimeter. The thermodynamic calculations in obtaining a $\Delta H$ of mixing are similar to those encountered in the ionic reaction experiment; the net heat capacity of the mixed product can be assumed to be the same as the sum of the heat capacities of the unmixed liquids.

The advantage of introducing a heat of mixing experiment of this type is that in addition to its thermodynamic aspects, a test for ideality of pairs of liquids can be demonstrated. Furthermore if the chloroform-acetone, the carbon tetrachloride-acetone, and the chloroform-carbon tetrachloride systems are studied on an equimolar basis, the results provide a good point at which to begin a discussion of hydrogen bonding.

Using two moles of the liquids mixed in a 665 -ml Dewar calorimeter at 25°C, there is a 13°C temperature rise for chloroform and acetone. The $CCl_4$—$CH_3COCH_3$ experiment indicates a drop in temperature of more than 1°C, while for the $CHCl_3$—$CCl_4$ system, the drop is less than 2°C. Thus, it is seen that the molecular interactions that cause the temperature rise in the chloroform-acetone system are of an order of magnitude greater than those involved in the other two systems. The departure from ideality may be classified as due to a weakening of the average attractive forces upon mixing in the cases of $CHCl_3$—$CCl_4$ and $CCl_4$—$CH_3COCH_3$, and as strongly in the direction of compound formation for chloroform and acetone. Other physical properties reflect this phenomenon. In particular, considerable deviation from Raoult's law exists in the direction of lowering of the vapor pressure in the chloroform-acetone system; this deviation is a maximum around 50 mole percent composition.

A specific hydrogen bond interaction between the hydrogen atom of the chloroform molecule and the oxygen atom of acetone has been advanced to explain the vapor phenomenon.[1] Thus the $\Delta H$ of mixing determined for the mixing of equimolar amounts of chloroform and acetone is related to the formation of a C—H···O bond and would equal the $\Delta H$ of bond formation, if in the absence of the C—H···O interaction the two liquids were ideal, if all of the chloroform and acetone molecules were bonded to each other in the equimolar mixture, and if all of these existed in the lowest vibrational state.

The $CHCl_3$—$CCl_4$ and $CCl_4$—$CH_3COCH_3$ information provides a strong indication that if the C—H···O interaction were removed, the chloroform-acetone behavior would be close to ideal. Both chloroform and acetone exhibit a similar behavior towards carbon tetrachloride. Moreover, they interact with carbon tetrachloride in a less vigorous way than they do with each other.

The average $\Delta H$ of mixing of chloroform and acetone as determined by students using reagent grade chemicals was $-.95$ kcal/mole. The Boltzmann distribution of molecules between two states is $n_2/n_1 = e^{-(\Delta E/RT)}$ where $n_1$ is the fraction of molecules in the lower energy state and $n_2$ is the fraction in the higher state. Suppose $\Delta E = .95/n_1$ kcal/mole; then, at 25°C, 86% of the molecules would exist in the lower state, and $\Delta E$ would equal 1.1 kcal/mole. It is certainly an oversimplification of the actual system to apply a Boltzmann distribution of one bonded state consisting of a hydrogen-bonded complex and one non-bonded state corresponding to separate chloroform and acetone molecules, but it is likely that most of the molecules are bonded at 25°C.

The entire question of hydrogen bonding between chloroform and basic solvents has recently been reviewed.[2] The interaction between chloroform and acetone in the liquid state may be considered to be intermediate between solution and reaction.

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# A Program of Research Projects in Chemistry for College Freshmen

As part of a plan for studying ways to improve the teaching of elementary chemistry to college freshmen, an experimental program of special research projects was carried out at The Johns Hopkins University during the academic year 1958–59 and the subsequent summer.[1] The goal was to study the feasibility of selecting from a group of freshmen a limited number of gifted students to work on research instead of the usual routine freshman laboratory course during the second term of the academic year. These research projects were selected with the aim of achieving significant results during six to ten hours of laboratory time per week for a period of fifteen weeks. Members of the chemistry staff volunteered to direct the research.

On the first of December, the plan was explained to all 300 students in the course and they were invited to submit proposals suggesting a problem and a plan for working on it, together with reasons why the project was interesting and why results obtained might be significant. It was explained that the purpose of this proposal was to test the students' thinking rather than to serve as a guide for the ultimate project. The students were told that the nature of the projects finally put in operation would be limited by the facilities of the laboratory and the funds available for the support of the work. Under these circumstances, it was felt that only a limited number of the projects proposed could be carried out and that some students selected for this work might be required to do their research along lines suggested by the faculty. Only one student actually undertook research on the problem he proposed. A number of the others, however, showed an intelligent, inquisitive, and thoughtful approach in working out proposals. In all, fifteen proposals were submitted by the students and these were screened on their merits and on the academic records of the authors.

The next step was a laboratory examination to test the students' ability in experimental work. Eight students were selected from the group which had submitted proposals and these men were given aqueous solutions containing a number of unknown cations and anions, each student receiving a different solution. They were then told to go into the chemistry library, study methods of qualitative analysis, and identify the unknowns. They had about three weeks to get the answers and had to do the necessary laboratory work in their spare time. Counting both substances present which were missed and substances reported which were not present, the students attained an average grade of 80 on this laboratory examination. This was surprisingly high in view of the fact that none of the students had previously studied any qualitative analysis. Moreover, the first term of the course in elementary chemistry at Johns Hopkins both in classroom and laboratory is concerned far more with chemical principles than with descriptive chemistry. Thus, these students had comparatively little background for carrying out these identifications in the laboratory and they showed remarkable initiative in studying the methods of qualitative analysis in the library completely on their own, and then carrying out the procedures, again without any help from the faculty.

On the basis of the laboratory examination, six students were selected for the special project program. Through consultation with the faculty, each student arrived at the choice of a project. Only one student worked on the project which he originally proposed, which was a study of the effect of growth stimulants on plants. The other projects included a study of catalytic reaction rates with the help of gas chromatography, a study of the effect of bombardment with radioactive particles on the surface resistance of semiconductors, a study of reaction rates in flames, and a study of mutual solubility in two-phase liquid systems. Each student was expected to put in between six and ten hours per week in the laboratory, together with consultation with the members of the faculty guiding the project. The facilities of the department glass-blower and shops were available to the students for the construction of special apparatus. Funds were provided for the purchase of equipment or instruments not available in the department stockroom. At the end of the school year in late May, the students were required to submit a report on the results obtained in their research. An effort was made through consultation to instruct the students in writing their research reports which were expected to be similar to theses or industrial research reports.

On the basis of results obtained and potential ability displayed, three of the students were selected for research fellowships which enabled them to continue their projects during the summer months of 1959. These students carried on more advanced work during this period and obtained results which will merit brief publications in the chemical journals.

On the whole, students showed imagination and a sense of judgment in solving problems in this experimental research at a level comparable with many first year graduate students. They displayed an ability to weigh questions of accuracy against questions of time and expense, and cleared up difficulties quickly

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[1] Funds for the support of this program were provided by the National Science Foundation.

enough so that the progress of the research went forward in a satisfactory manner. The students worked hard and were enthusiastic. They developed an insight into chemistry and a feeling for carrying on chemical inquiry far beyond what had been expected of men at this level. Thus, we conclude that the gifts are there for the developing; there is no doubt that ingenuity, insight, and eagerness are present in the youthful mind and ways can be found to make it fruitful; with proper stimulation the best of freshmen can be led to do reasonably successful research in spite of an apparent possible lack of a general background in chemistry. We also conclude that they cannot be expected to find problems for study by themselves, but have the ability to pursue a chemical study with only a limited amount of direction.

### Conclusion

Finally, we would like to make suggestions and raise a few questions.

It is not difficult to conceive that the most gifted students, those with high I.Q.'s and excellent scholastic records, are more susceptible to this stimulation and cultivation. But how much of this superior intellect is required to make good research men? At what lower level of I.Q. is encouragement and stimulation ineffective or inefficient?

The type and magnitude of the problems offered in such a program bear close scrutiny:

- Is the problem of sufficient importance and stature to satisfy a serious research worker?
- Is there a good chance, at least 50–50, that it can be brought to a satisfactory conclusion within the allotted time?
- Is it within the capability of the student?
- Is it a straightforward problem or is it nebulous and obtuse?
- Is it stimulating, or only a tedious string of routine measurements?

The student is stimulated most and sustains interest best in problems which do not strain his capabilities too much, but which are of such a scope that he can really identify them as his own, and from which he can expect to see real concrete results.

How will these students fare in their future educational careers, and what benefit is this program to them? It is conceivable that the standardized engineering and science courses which follow the freshman course in elementary chemistry may be so routine and unimaginative as to degrade the momentum of interest which such a freshman research program stimulates. However, we feel that it was clearly demonstrated in this experiment that a limited group of top students can be given great stimulation at this level and we believe that thought should be given to the design of the program of study in subsequent years so that this momentum is not lost.

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# Color Photography of Spectra

The emission spectra of excited atoms and molecules are one of nature's most beautiful and inspiring spectacles. In the multitude of colored spectral lines nature reveals to us some of her most intimate secrets. Unfortunately, many students of science do not have the good fortune to see a spectrum first hand. Most of the spectral photographs made each day are in black and white, and understandably so, since most of the lines used in analytical work are in the ultraviolet region of the spectrum where prism dispersion is greatest. The pictures of spectra reproduced in most books leave much to be desired, the plates being so small and poorly reproduced that most of the detail, color and immediacy of the real spectra are lost.

The advent of the new high-speed color films which can be processed by the user has made color photography of spectra a practicality. Using a relatively inexpensive spectrograph, students with no previous experience at color photography can turn out beautiful full color transparencies of spectra, which can be viewed by a group, in less than two hours. The choice of spectrographic instrument is dictated by several factors, the most important of which are cost and the instrument's ability to accept standard 35-millimeter color film. Most prism spectrographs are unsuitable since they have inherently poor dispersion in the visible, and they dictate the use of glass plates which are not generally available for color photography. A medium sized grating instrument such as the Bausch & Lomb 1.5 meter Stigmatic Instrument is well suited to color photography of spectra. The visible portion of the spectrum is spread out to a length of about 9 in. which is entirely adequate to show good separation of major spectral detail.

Because the grating spectrograph uses 12-in. strips of film it would be impossible to have them processed commercially due to the difficulty in handling such short lengths of film on a production basis. This makes it essential that the user process his own spectral films. Of the various color films on the market, the new high speed films with ASA exposure ratings of 100 or 150 are most suitable for spectral photography. The film may be purchased in standard 36-exposure cassettes or, if much work is anticipated, in more economical 50- or 100-ft. rolls. The exposed strips of film may be proc-

essed conveniently in an inexpensive 16-ounce plastic reel-type developing tank. Kits of chemicals which will process four 36-exposure rolls of color film are available from most photographic dealers for under two dollars. One 36-exposure roll of film will supply enough film for 4 or 5 loadings of the spectrograph film holder. The finished films are ready to view about 1½ hours after processing is begun.

### Technique

A tungsten lamp, the kind used for microscope illumination, placed about one foot from the slit and defocused so that the filament image is not visible, makes a good source for a series of trial exposures. A wide range of exposure times will show at a glance the effects on color rendition of under and overexposure. A test exposure which shows a wider band of yellow on the film than the eye sees on a piece of translucent paper placed over the focal plane is overexposed.

The results of tests run on a number of different sources are given in Table 1. It should be noted that for a given experimental setup these exposure times may have to be modified to suit existing conditions. Since a grating instrument forms a number of spectral systems (orders) which overlap one another, it is advisable to use an ultraviolet absorbing filter to remove any overlapping UV lines which might confuse or degrade the images. This precaution is especially important in the photography of quartz mercury arc or carbon arc spectra which are rich in ultraviolet wavelengths. Any filter which cuts off below 3600 Ångstroms is suitable.

The emission spectra of gases are obtained from capillary-type high voltage discharge tubes. Tubes filled with various gases can be obtained commercially from a number of sources.[1] It is also possible to construct your own tubes, provided you have some glass blowing skill, wire leads, a good vacuum system and a supply of the necessary gases. The tubes are built, evacuated, baked out and are slowly filled while connected to a high voltage transformer. After a number of tries, the gas pressure which gives the best discharge can be determined and the tube sealed off and "pulled" from the vacuum system. It is also possible that a local neon sign shop could be persuaded to make (and possibly donate) some small discharge tubes. While gas discharge tubes may be operated by touching a spark coil to one end and grounding the other, a much more satisfactory method is to run them from a high voltage, low current transformer capable of delivering about 4000 v. Used neon sign transformers, which are ideal for the job, can be obtained from sign shops for a few dollars. With the transformer primary connected to a variable autotransformer the secondary voltage may be adjusted for optimum light output. The voltage should be adjusted to the minimum value that will maintain a stable discharge. Excess voltage will only shorten tube life due to electrode material sputtering onto the glass with resultant loss in light intensity. Ordinary spark plug wire is quite satisfactory for making connections between the lamp and the high voltage transformer. All exposed connections should be covered with rubber tubing and plastic electrical tape to reduce the possibility of electrical shock.

Setup for making color photographs of gas discharge spectra. Robert Linck is shown pressing a button which prints a reference mark on the end of the film strip. In actual practice exposures are made in darkness to prevent stray light from entering the spectrograph slit.

[1] Tube Light Engineering Company, 427 W. 42nd Street, New York 36, N. Y.

**Table 1. Typical Exposure Data for Color Photography of Spectra[a]**

| Light source | Approx. voltage | Exposure time | Filter used | Characteristic features of the spectrum |
|---|---|---|---|---|
| Tungsten lamp (100 watt) | 115 | 1.5 sec | None | Continuous spectrum |
| Fluorescent lamp | 115 | 10 min | None | Continuous background with sharp Hg lines superimposed |
| Mercury arc (quartz) | 115 | 15 sec | UV absorb. | Yellow, green and blue Hg lines |
| Neon tube | 3000 | 12 min[b] | Cyan | Many different colored lines, second order blue lines |
| Helium | 3000 | 9 min | None | Sharp lines of a variety of colors |
| Nitrogen | 3000 | 12 min | None | Complex band systems of $N_2$, many colors present |
| Carbon dioxide | 3000 | 15 min | None | Band systems, especially in the green |
| Hydrogen | 3000 | 10 min | None | First two Balmer lines, red and blue-green |
| Mercury-argon | 3000 | 5 min | None | Yellow, green and blue Hg lines |
| Iodine vapor (absorption)[c] | ... | 1.5 sec | None | Absorption band system of $I_2$ against tungsten continuum |
| Neodymium ammonium nitrate solution (absorption)[d] | ... | 1.5 sec | None | Sharp absorption bands in yellow, green, and blue regions of spectrum |
| Arc spectra | ... | ... | UV absorb. | Bright lines and series |

[a] Photographed with a Bausch & Lomb 1.5 meter Stigmatic Grating Spectrograph. Data are for Super Anscochrome Daylight-Type ASA 100 roll film. For other films, multiply exposure times by 100/ASA film rating. Filters used were No. 7380 UV Absorbing and No. 5031 Cyan, available from the Corning Glass Works, Corning, New York.

[b] Expose 6 min without filter, 6 min with Cyan filter.

[c] Iodine crystals are placed in a long, evacuated Pyrex cell. The cell which should be at least 20 cm long may be heated with heating tape to increase the vapor density. A tungsten lamp is used as light source.

[d] A few crystals dissolved in a 10-cm cell will give good absorption. Tungsten lamp source.

The discharge tubes should be positioned in front of the slit so as to give the brightest image when looking directly at the grating. Since the lines in a discharge spectrum may vary widely in intensity, it is often necessary to overexpose a group of bright lines to get sufficient exposure for a group of faint ones. Exposing for the faint green and blue lines of neon will cause sufficient exposure in the red lines to record the diffraction patterns associated with these intense lines. The central maxima in these patterns may appear yellow instead of red due to local overexposure. Sometimes spurious "ghost" lines will be recorded next to a particularly intense line such as the green line of mercury. In many of the spectra faint bluish lines may be seen at the red end of the spectrum, illustrating as no other method could the way in which the second order grating spectrum overlaps the first order.

Colored filters can be used to advantage to even out the intensities of the lines and improve color balance. The procedure, which works best with groups of lines at opposite ends of the spectrum, consists of first giving proper exposure to the strong lines, after which a filter is inserted which absorbs the strong lines and transmits the faint ones. The exposure is then continued until the faint lines have received sufficient exposure. For critical work it may be advisable to use color balancing filters to compensate for the failure of the reciprocity law for long exposures at low intensities. The color emulsions tend toward the blue when used under these conditions. Information can usually be obtained from the film manufacturer as to which filter combination is recommended.

Color processing solutions should be made up according to manufacturer's instructions, stored in airtight amber bottles, and used within two weeks. The instructions for the particular color process used should be followed carefully, especially as regards time and temperature. Processing may be expedited by developing more than one film at a time. Two or three film strips may be exposed, stored in a light-tight can and then taped together end to end and threaded into the processing reel in total darkness. Extreme care must be taken to insure that the film strips do not jam or overlap in the reel as this will cause faulty processing. Films must be handled with care at all times to avoid scratches, finger marks and dust spots. Dry film strips should be placed between clean white paper and pressed in a heavy book to prevent curling.

In addition to the photography of lamp and gaseous discharge spectra, there are also a number of other interesting applications to which the color technique may be applied. If light from a tungsten lamp is sent through the spectrograph slit after first passing through a glass cell containing colored solution, one obtains a color photograph of the absorption spectrum of the solution. Such a spectrum, which may also be made for gases, consists of one or more dark regions superimposed on an incandescent continuum. If a simple chlorophyll extract is used one can readily photograph the red and blue absorption bands of this most important natural dye molecule. The neodymium spectrum may be photographed by interposing the lens of a glass-blowing goggles between the lamp and the slit. These glasses, which contain neodymium compounds, make use of the very strong, narrow absorption band in the yellow to remove much of the annoying sodium light.

If a carbon arc is used as a source the emission lines of compounds placed on the electrodes may be photographed. Salts of the alkali metals show systematic differences in their spectra as they increase in atomic number. The stepped diaphragm incorporated in most spectrographs can be used to record the alkali series on the same strip of film for comparison purposes.

Another interesting experiment would be to make a color photograph of the solar spectrum. The spectrograph would have to be moved to a window where the direct rays of the sun could be focused on the slit by means of a simple system of lenses and mirrors. With the proper exposure one should be able to see many of the Fraunhoffer lines (the absorption spectrum of the relatively cool solar atmosphere).

### Viewing the Spectra

There are a number of ways to view and display the finished color spectra. For permanent display purposes a number of film strips taken with full slit height can be mounted on a sheet of photographer's opal glass illuminated from the rear. If a spectrum comparator is available which accepts 35 mm film, one can observe the film greatly enlarged, a small section at a time, on the comparator screen. This produces a beautiful sight but is limited to viewing by a small group in a fully darkened room. Unfortunately, lantern slide projectors are not made which will project a 10-in. strip of film at one time. Films can, however, be cut into strips, mounted in $3^1/_4 \times 4$-in. cover glasses, and projected in a standard lantern slide projector. It is also possible to construct a special slide carrier which holds $2 \times 10$-in. slides. Films sandwiched between $2 \times 10$-in. cover glasses are placed in the long holder and then slid along until the whole plate has been scanned.

For viewing the spectra without a projector it is possible to make large positive color prints. The films can be enlarged and printed on transparent, translucent or opaque positive color material. The transparent base materials are viewed by transmitted light, while the translucent and paper base materials are viewed by reflected light. The films, which are available in sizes up to $11 \times 14$ in., can be cut into strips, exposed in an enlarger, processed and mounted end to end over a long translucent box illuminated with fluorescent tubes. The color printing materials require much the same steps as are used in processing the original films except on a larger scale, in trays.

A commercial spectrograph, while highly desirable, need not be the only means of photographing the spectra. With a little ingenuity and a few optical parts, a spectrograph could be constructed which would do a reasonable job. Whatever the spectrographic equipment used, the results are bound to be gratifying and well worth the effort to add the exciting dimension of color to the curious spectral lines.

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*Laboratory safety, III*

# Accident Procedures

It is impossible to prevent all accidents in educational laboratories. Despite well organized and carefully followed safety programs, despite highly trained, safety-conscious personnel, despite the use of modern, ingenious, and effective safety devices, accidents will occur. It is the purpose of this article to consider procedures which will minimize the effects of accidents and safeguard both life and property.

Two points will be emphasized in this discussion of effective emergency procedures: first, the person confronted with an emergency situation does not stand alone; second, there is a need for quick, correct, and decisive action in meeting the emergency.

Many people, face to face with an emergency, experience a horrible feeling of "aloneness." Suddenly a new situation has been presented—a situation which demands an immediate and correct response— and the responsibility for this response falls upon their shoulders. The teacher or research man must realize that he is not alone, depending solely upon his own devices to counter the emergency. In both metropolitan and rural areas trained police and fire-fighting forces, ambulance and hospital services, emergency utility crews, are available and need only be notified in order to swing into action. Even within a particular laboratory or school, help is available from other research people, teachers, or students. Thus, the cardinal rule for handling emergency situations is simple—get help.

That action in meeting emergency situations must be quick, correct, and decisive is perhaps too obvious to belabor. Action taken during the first few minutes in attempting to extinguish a fire or to stop severe bleeding often determines whether the emergency can be handled easily or will make black headlines in the next day's newspapers. Further, incorrect procedures are worse than useless; usually, these aggravate the emergency, not relieve it. Finally, action must be decisive. Halfway measures may check the emergency momentarily but will leave a worsened situation if not followed up effectively.

Quick, correct, and decisive action does not happen of its own accord. The first step in insuring such action involves careful planning long before the emergency situation arises. Each teacher and each research student must continually ask himself "What would I do—if this distillation caught fire—if a student cuts himself severely in this laboratory—if this laboratory had to be evacuated and that door were blocked?" A well-thought-out plan of action prevents panic and loss of time in meeting any emergency.

Not only must there be a plan, but the plan must be feasible—and correct. The proper fire extinguisher must be available before it can be used; a first aid kit must be stocked before first aid supplies can be used in an emergency. Further, the man facing the emergency must be trained in the use of the fire extinguisher or the first-aid kit.

Above all, the plan and the emergency equipment must be adequate for the job at hand. A five-pound carbon dioxide extinguisher is fine for a small fire, but useless if an entire hood becomes enveloped in flame; one or two bandaids will be adequate for minor cuts or scratches but of little value in stemming the bleeding from a severed artery.

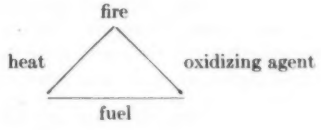
The following discussion of fire fighting and first aid will attempt to indicate the type of planning and training necessary, the type of equipment required, and some of the techniques effective in meeting laboratory emergencies.

## Fire Fighting

Three classifications of fires are recognized:

*Class A*—Ordinary combustibles such as paper, wood, clothing, etc. These are best extinguished with water.
*Class B*—Flammable liquids such as petroleum products, benzene, etc. These are best extinguished with $CO_2$ or dry chemicals.
*Class C*—Electrical apparatus. These also are best extinguished with $CO_2$ or dry chemicals.

Three factors must be present in order for a fire to occur: a source of ignition (heat), a fuel, and an oxidizing agent.




The proper combinations of these three factors will cause a fire; the fire can be extinguished by breaking any side of the fire triangle: remove the fuel or separate the fuel from the oxidizing agent, dilute the oxidizing agent, or cool the system.

In order to handle the various types and intensities of fires encountered in the laboratory, a "defense in depth" should be organized. The first line of this defense is the five-pound carbon dioxide fire extinguisher, the fire blanket, or the wet rag immediately available in the laboratory at the site of the fire. Most fires will be controlled with these devices.

The second line of defense is composed of the larger, less portable 15-, 20-, or 50-pound carbon dioxide extinguishers which should be placed at centrally located points throughout the laboratory building. The smaller extinguishers brought from other laboratories to the fire scene are important contributors to this second line.

The third line of defense is made up of the large capacity dry-chemical extinguishers and the soda-acid extinguishers. The dry-chemical extinguisher has a tremendous fire-killing capacity, but cleanup is messy. Dry-chemical extinguishers should be used only when a relatively large fire is involved or when the hazard warrants the difficulty in cleanup.

Several points should be noted in considering fire fighting in the laboratory. First, the city fire department, trained professionals, must be notified immediately of all but the most minor fires. Be prompt in notifying the fire department, give explicit directions as to the location and extent of the fire, detail one man to direct the fire department to the site of the fire, and be prepared to assist the firemen by warning them of the presence of any hazardous materials (e.g., sodium, large quantities of solvent, etc.). Again and again, reports of major fires include the phrase "alarm delayed while occupants tried to control the fire with fire extinguishers." The fire department would rather make one hundred runs and find the fire extinguished than to be called to a roaring blaze, out of control because someone felt that "we can handle this ourselves." Call in the alarm!

Second, laboratory personnel must be trained in fire-fighting techniques, must know the location of extinguishers, and must be taught to bring the heavier fire-fighting equipment to the scene of the fire. Carbon dioxide extinguishers are ideal for most laboratory fires. However, the effective range of this extinguisher is limited and the supply of $CO_2$ is exhausted rapidly (45 seconds or less even for the large 20-pound units.) Untrained personnel tend to fight a fire from too great a distance or else scatter the fire by too direct an attack. Thus, the untrained laboratory man will require a larger quantity of carbon dioxide to extinguish a particular fire than will a trained individual. The fire department will be glad to assist you in the demonstrations or practice exercise which should be an integral part of any effective training program. The major fire-equipment manufacturers (Kidde, Ansul, etc.), have films available which will help in a training program, supplementing but not replacing the practice exercise.

### *General Rules for Fire Fighting*

The first concern in fire fighting is not to kill the fire but to keep the fire from killing or injuring anyone. Property can be replaced, lives cannot, so evacuate all non-essential personnel from the fire scene immediately.

If the fire gives *any* evidence of getting away from control of the extinguishers or if an explosion is imminent, get out of the fire area. As you leave, be sure that no one is left behind, shut all windows and hoods, and close the door. Once you have closed off the fire scene never, under any circumstances, attempt to re-enter the blazing room. The sudden influx of air as you open the door will probably set off an explosion. There are no research notes, spectra, or compounds valuable enough to warrant gambling a life in attempting their rescue.

Adequate respiratory protection with a gas mask will probably be necessary in order to fight any but the smallest laboratory fire.

Do not try to be a hero. When a fire occurs, get help. Yell! This should bring other people, with extinguishers, to your aid. Size up your fire situation carefully; call the city fire department for anything but the smallest blaze; be prepared to get away from the fire scene should the fire get out of control.

## First Aid

The term "first aid" means exactly that: the first aid that is given to an injured person before professional help is available. Fortunately, many of the accidents in the teaching and research laboratories are minor and "first aid" may be the only aid required. The teacher, graduate teaching assistant, and the research man should be able to administer first aid with a reasonable degree of skill and, more importantly, to decide when additional aid is necessary. The general rules are simple: keep calm, get help, stop bleeding, watch for shock.

### *Treatment of Cuts or Other Skin Wounds*

For small cuts, the danger from loss of blood is slight—the danger from infection is great. Clean the cut and surrounding areas with soap and water, examine the cut carefully for any slivers of glass, and brush them out with a piece of sterile gauze. Allow the cut to bleed freely since the flow of blood will help wash any bacteria from the wound. (Punctured wounds, with little bleeding, are particularly prone to infection and should receive professional aid.) Once the wound is cleaned, apply a little antiseptic and bandage.

Large, deep, and profusely bleeding wounds may indicate that an artery has been severed. Stop the bleeding and get a doctor. Place a thick pad of sterile gauze directly over the wound and press firmly. If the cut is in the victim's hand, keep the hand elevated. If direct pressure does not work, apply pressure to the appropriate "pressure point," the point between the wound and the heart where the artery lies near the surface and close to the bone. If neither direct pressure nor "pressure point" will stem the bleeding, apply a tourniquet between the wound and the heart. Use a piece of rubber tubing, a necktie, or any other piece of wide, smooth-surfaced material. Always inform the attending physician that a tourniquet has been applied and never cover the tourniquet with a bandage.

### *Treatment of Burns*

Burns, either from flame, hot objects, or chemicals, are classified as first degree (reddening of the skin as in minor sunburn), second degree (formation of blisters), and third degree (charring of the flesh or other deep and extensive tissue destruction).

First and very minor second degree burns (small blisters as might be caused by picking up hot tubing) can be treated in the laboratory. Cover the area with a sterile petroleum jelly or burn ointment and protect with a bandage. If the burn is caused by chemicals, flush the area with copious volumes of water, then with a 5% $NaHCO_3$ solution in the case of acid burns or a saturated solution of boric acid in the case of caustic burns.

Extensive second degree burns, burns in which the blisters have opened, and third degree burns cannot be treated by the laboratory man. *These burns must receive prompt professional care.* Treat only for shock. The greater the area of the burn and the greater the severity, the greater will be the pain, fluid loss, and hence shock.

### *Treatment of Shock*

Shock, or physical collapse, may occur in every injury. The degree of shock will depend upon the nature and severity of the injury and upon the victim's own physical and emotional makeup.

The symptoms of shock may include trembling, a pallor of the face or lips, difficulty in breathing, faintness, and nausea. The pulse may be weak, the hands and feet cold, and a cold, clammy sweat may appear. One or all of the symptoms may occur, either slowly or suddenly. In every injury, no matter how slight, watch for these symptoms and be prepared to act.

Treatment should include the following: lay the victim flat, head low and feet high. Stop any bleeding and keep the victim warm with blankets, lab coats, etc. Smelling salts, spirits of ammonia, or amyl nitrate vapors may be administered by inhalation. If, and only if, the victim is conscious, give warm sweetened drinks. Remember, in severe shock, you are dealing with a very serious condition which can prove fatal although the injury causing the shock is minor. Get professional help immediately.

Many individuals as they anticipate treating an injured person, may experience some symptoms of shock themselves. Often these symptoms disappear when actual treatment of the injury starts. However, if there is any doubt that the first aid treatment can be continued, turn the job over to someone else and get out of the way.

#### *Eye Injuries*

Injuries to the eyes are all too common. The best first aid measure is to prevent such accident by enforcing laboratory safety rules.

Chemical splashes: flood the eye with water—when you think that you have done enough washing, do it again. Cover the injured eye with a sterile gauze pad and get professional help immediately.

Other foreign objects: if the eye does not appear to be damaged, wash the eye with eyewash solution or boric acid solution or get professional help if necessary. In case of physical damage to the eye, cover the eye with a sterile pad and get professional help.

You cannot be too careful in treating eye injuries. If one eye is affected, assume that both eyes are involved and treat both. If chemicals splash or glass is thrown near the eye, assume that the eye has also been involved.

#### *Poisoning*

Poisonous materials are found in the laboratory and may be taken into the body through the lungs, by absorption through the skin, or through the mouth.

Toxic vapor poisoning: remove the victim to fresh air, apply artificial respiration if breathing has stopped, treat for shock, and get help immediately in anything but the most minor accident.

Poisoning by mouth: for strong acids or bases, do not induce vomiting. Give a demulcent drink such as egg albumen, milk, or mineral oil. For other poisons, give the antidote as described on the label of the bottle.

#### *General Rules for First Aid*

Even the most highly competent physician is not a mind reader, nor is he able to treat an injury successfully without knowing the nature of the material which caused the injury. The chemist must be prepared to describe the cause of injury and to explain the chemistry of the particular material (hydrolysis reaction, etc.). Hence, never send an injured person alone to the physician; take him.

Call ahead before taking an injured person to the hospital or Health Service. Explain the extent, nature, and cause of the injury. Forewarned, the hospital will be able to react more quickly and efficiently to the emergency situation.

Determine, and make known to all personnel, the proper procedures for getting outside help at any hour of the day or night, on week days or on week ends. A list of emergency telephone numbers is invaluable and should be placed in the hands of all teachers, research directors, graduate students, maintenance people, and stockroom men.


#### Acknowledgment

The author wishes to acknowledge, with deep thanks, the assistance given by Drs. A. B. Denison and T. George Bidder of the Western Reserve University Medical School, by Battalion Chief James A. Mitchell and Captain Ed Masak of the Cleveland Fire Department, and by the Research Department, Koppers Company, Inc.


## *Division of* CHEMICAL EDUCATION

*American Chemical Society*

### New Office for the Examinations Committee

The Examinations Committee of the Division of Chemical Education has been moved to the University of South Florida. All correspondence and orders should be addressed:

Examinations Committee—ACS
University of South Florida
Tampa, Florida

Dr. T. A. Ashford, chairman of the committee, recently accepted a position with the University and has transferred the test office to the new location. The University has generously provided ample space in its new Science Building to house the office staff and the stock of test booklets.

Teachers interested in the testing program of the Examinations Committee of the Division of Chemical Education are invited to write directly to Dr. Ashford for further information.

*The following test forms are now available:*

General Chemistry Forms 1960, 1958, 1958S, M, MS, K, and G
Qualitative Analysis Supplement to General Chemistry Form J
Qualitative Analysis Forms 1960, H and Y
Quantitative Analysis Forms N and G
Organic Chemistry Forms 1958, H, Y, and MB
Physical Chemistry Form L
Biochemistry Form 1959
High School Forms 1959, 1959S and N

*By March 1961, four new tests will be available:*

Organic Form 1961
Organic Form 1961B (for a brief course in organic chemistry)
High School Form 1961
Inorganic Form 1961 (the first test in an entirely new field)

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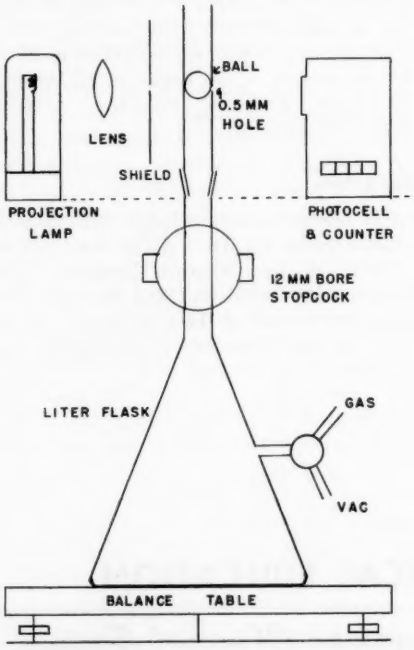
# Maintained Oscillations for the Bouncing-Ball Determination of Cp/Cv

The conventional bouncing ball experiment for measuring the heat capacity ratio suffers from the limited number of oscillations which the ball can be made to perform.[1,2] A modification has been suggested by Kohler[3] for research purposes in which the ball is maintained in continuous oscillation. We have found that this method can be readily adapted to the undergraduate physical chemistry laboratory. Accurate results are easily obtained, and the continuous nature of the oscillations adds to the curiosity of the experiment.




The apparatus is shown in the figure. A three-way inlet valve is attached to the side of a one-liter flask, and a 12-mm bore stopcock is attached to the neck. This large stopcock can be omitted, but it does aid in filling the system with different gases. A standard taper 19/38 female joint is sealed to the other side of the stopcock. Precision bore tubing[4] was selected to provide a smooth but close fit with a $^5/_8$ precision stainless steel ball bearing.[5] A short length of this tubing is attached to the male standard taper joint.

The maintained oscillation of the ball in the precision bore tube is accomplished by gas flowing through a small (0.5-mm diameter) hole, which is drilled through the wall of the tube. A satisfactory way to make this hole is to chuck a short length of No. 24 hypodermic needle tubing in a small drill press and drill the hole by using a paste of carborundum and turpentine. By supporting the glass directly beneath the drilling region, a clean hole can be made with only a small amount of chipping.

A slow flow of gas is adjusted so that the ball continues to oscillate about the region of the hole. A swing of about two centimeters is easily maintained by the valvelike action of the ball and hole. Kohler has shown that the effect on the small hole of the frequency of oscillation is very small, and only for very accurate measurements need a correction be applied.

The application of the apparatus requires filling the system with the gas to be measured, placing the ball in the top end of the tube, and adjusting the gas flow to the point where a steady oscillation is obtained. The frequency is measured by counting the number of oscillations for a given period of time. A sufficient number of oscillations is taken so that the frequency can be determined within 0.5%. We have incorporated a photocell counting system to reduce the tedium of this counting process and to eliminate the possibility of counting errors. A simple photocell relay[6] is attached to a 110-v counting relay.[7] The interruption of a beam of light by the bouncing ball trips the counter, and time for a given number of counts is taken by a stopwatch. An adjustment of the precision bore tube to the near vertical position is facilitated by using an old balance platform to support the apparatus.

The simplified theory of operation of the bouncing ball experiment is found in Schufle's article,[1] and a complete discussion of the various correction terms to achieve the highest accuracy is given by Kohler.[3] To the first approximation, the ratio of heat capacities is given by

$$\gamma = \frac{4\pi^2 m V f^2}{PA^2}$$

where $V$ is the volume of the system, $m$ the mass of the ball, $f$ the frequency of oscillation, $P$ the internal average pressure, and $A$ the cross section area of the tube. A typical set of data on air, taken with our apparatus, is $V = 1164$ cc, $m = 16.31$ g, $A = 1.970$ cm$^2$, $P = 63.0$ cm Hg, $f = 247$ counts/100 sec, $\gamma = 1.40$. The over-all accuracy of this method is inherently within 0.1% if correction terms are developed. The simplified theoretical treatment gives an accuracy around 1%.

[1] Schufle, J. A., this journal, **34**, 78–80 (1957).
[2] Richardt, E., *Physik. Z.*, **30**, 58–9 (1929).
[3] Kohler, W. F., *J. Chem. Phys.*, **18**, 465–72 (1950).
[4] This glass was obtained from Fischer and Porter, Hatsboro, Pa., and we wish to acknowledge their assistance in selecting the tube.
[5] Precision ball bearings were purchased from Hoover Ball and Bearing Co., Ann Arbor, Michigan.
[6] Nitelighter, Fischer-Pierce Co., Boston 5, Massachusetts.
[7] An inexpensive relay may be obtained from Herbach and Rademan, 1204 Arch Street, Philadelphia 7, Pennsylvania.

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# Quantum Mechanics for Organic Chemists

Although much of the modern theory of organic chemistry derives directly from the results of quantum mechanics, few organic chemists have any but the most superficial acquaintance with this powerful and potentially useful discipline. In part this lack can be attributed to the practical difficulty of including quantum mechanics as part of the graduate course of study for the organic chemist, especially in relatively small schools which are unlikely to have a large enough staff to offer a wide gradation of specialized courses. As a rule the graduate student who elects organic chemistry does not have an extensive mathematics and physics background, and even were this not the case, the only course available in quantum mechanics is all too frequently one which concentrates on the formalism of the discipline and stops short of the realm of application to meaningful chemical problems. At best, the student finds such a formal approach "interesting" but scarcely practical with regard to application toward the problems of the reaction flask. Even the common "quantum chemistry" course, since it is usually oriented toward physical chemists, must consist to a large degree of mathematical formalism—application to chemical problems, if considered at all, is left to the end of the course. What appears to be needed is a short course in quantum mechanics which keeps the mathematical formalism to a minimum and plunges as quickly as possible into such simple and useful applications as are associated with molecular orbital theory and valence bond (bond orbital) theory.[1]

The writer feels that such an approach will demonstrate at the very outset the fact that quantum mechanics does relate to simple but non-trivial problems of organic chemistry, and that it does so with the use of suprisingly little mathematical apparatus. A student taking such a course will most certainly not acquire any great facility in the solving of problems involving the molecular orbital or valence bond theories, but he will be made aware by concrete example that here is a tool with promise. For many of the better students this will provide sufficient motivation for further pursuance of quantum mechanics, whereas a more formalized treatment might well have stifled further curiosity for virtually all of the students.

A course similar to the above has been taught at the University of New Hampshire during the second semesters of the 1957–58 and 1959–60 academic years. The only difference from the course proposed in the preceding paragraph is that our course contains physical and inorganic majors in addition to organic chemists. For the physical chemists the quantum mechanics serves as a preview to a year course in theoretical chemistry in which the formal aspects of quantum theory are presented in greater detail.

Our short course in quantum mechanics takes up slightly more than one-third of a semester of advanced physical chemistry required of all doctoral candidates. The remainder of the course consists of atomic and molecular spectra and statistical thermodynamics. Much of the quantum theory can thus be carried over for further application throughout the semester.

### Material Covered

The first week (3 one-hour lectures) is devoted to a presentation of the basic postulates of quantum mechanics, i.e., the significance of the state function, the Schrödinger wave equation, definition of expectation value, normalization and orthogonality, a little about operator algebra, the uncertainty principle, the exclusion principle, and the complementarity principle. Thereupon the student is immediately exposed to the free electron model for straight chain and cyclic conjugated systems. This introduces the student to quantized energy levels, explicit wave functions, normalization and orthogonality, and probability interpretation although not introducing any complicated mathematics. Within this simple framework one can discuss the electronic absorption spectra of conjugated molecules and even make a reasonably quantitative calculation of the maximum wavelength of absorption. Bond orders and atom electron densities may also be introduced in a semiquantitative fashion. Problems are assigned involving such molecules as 1,3,5-hexatriene, the cyclopentadienyl anion, and carotene. As is done throughout the course the student is encouraged to read some of the original literature. Most students find the papers of Kuhn (*1*), Bayliss (*2*), and Platt (*3*) not too difficult to appreciate. Wheland's (*4*) discussion of the free electron model has also been found quite efficacious as a lecture supplement.

The next topic involves a very brief sketch of the solution of the Schrödinger equation for the hydrogen atom, i.e., the equation is written down in Cartesian coordinates and in polar coordinates, separation of variables is indicated, and the form of the final solutions for $s$- and $p$-type orbitals given by

$$\psi_s = f(r)$$
$$\psi_{p_x} = f(r) \sin\theta \cos\phi$$
$$\psi_{p_y} = f(r) \sin\theta \sin\phi$$
$$\psi_{p_z} = f(r) \cos\theta$$

[1] The author is well aware that a great many graduate schools, particularly the larger ones, have incorporated quantum mechanics into the curriculum for organic chemists and that many have done so in a more efficient manner than that proposed in this paper. However, by virtue of personal experiences and contacts it is felt that a large number of smaller graduate schools consider the inclusion of such a course as an unnecessary or impractical extra. Part of the purpose of this paper is to insist otherwise.

As an outside assignment the student is asked to sketch these orbitals in the *xy*-, *xz*-, and *yz*-planes assuming some arbitrary value for $f(r)$.[2] The student is also asked to use these wave functions for eigenvalue problems involving simple operators and to prove their mutual orthogonalities. Reference is made to a text such as Pauling and Wilson (*5*) where explicit forms of these orbitals are tabulated.

The concept of hybridization is approached by deduction from experimental bond angles and configurations. Tetrahedral, trigonal, and digonal hybrids are constructed in a crude geometric fashion. As a student exercise the class is given the shapes of *d*-orbitals and asked to sketch hybrids involving such orbitals. The student is shown how to express these hybrids mathematically, e.g., by the linear combination illustrated by

$$\psi_{sp}{}^3 = \frac{1}{2}(\psi_s + \sqrt{3}\psi_p)$$

The significance of the orbital coefficients is related to percentage *s*-character, etc.

The problem of approximating a wave function is prefaced by a statement and simple proof of the variation theorem. The L.C.A.O.-M.O. (Linear Combination of Atomic Orbitals-Molecular Orbital) method is discussed first using hydrogen-like wave functions. The method is demonstrated for a hypothetical diatomic molecule A-B, and the requirements necessary to obtain a stable bond are discussed. Symmetry with respect to the bonding axis ($\sigma$, $\pi$, $\delta$, etc.) and with respect to the center of the molecule (gerade and ungerade) is discussed. Bonding and antibonding orbitals and the Aufbau principle for diatomic molecules are introduced. As student exercises the electronic structures of such molecules as $O_2$, $N_2$, CO, and NO are worked out. Reference is made to the literature, e.g., the paper of Long and Walsh (*6*) concerning CO and $N_2$. The L.C.A.O.-M.O. treatment of the *pi* electronic structure of ethylene is assigned. The significance of coulombic, resonance, and overlap integrals and their evaluation is briefly discussed.

Next the L.C.A.O.-M.O. method is applied to benzene and the symmetry of the molecule used to factor the secular determinant and to obtain the normalized eigenvectors. The solution of cyclic and non-cyclic determinants by use of the trigonometric formulas is given as an aid to problem computation (*7*). Total electron charge densities, mobile bond orders, free valence numbers, and localization energies are defined and worked out. Free valence numbers and localization energies are discussed with respect to addition, substitution and elimination reactions, and acid-base strengths using eigenvectors found in the literature for alternant hydrocarbons. As student exercises, molecular orbitals are constructed for such simple molecules as 1,3-butadiene, cyclobutadiene, and cyclopentadienyl anion. The chemical reactivity of butadiene is explained on the basis of the free valence numbers or localization energies. The student is referred to a paper by Coulson (*8*) for the relationship between bond order and bond length.

[2] It is probably advisable to point out that $f(r)$ is not the same for all of these orbitals. Of course, assuming so does not change the general forms of the orbitals.

The valence bond method is illustrated by the hydrogen molecule. Charge densities, bond orders, and free valence numbers are defined and distinguished from the molecular orbital definitions. Students are given valence bond wave functions (obtained from the literature) for such molecules as furan and naphthalene and asked to calculate charges, bond orders, and free valence numbers. Questions concerning the chemical reactivity of such molecules are interpreted on the basis of such reactivity indices. The relationship of valence bond theory to the resonance theory of organic chemistry is briefly discussed.

Throughout the course reference is made to selected sections of such texts as Pauling and Wilson (*5*), Kauzmann (*7*), Pitzer (*9*), Coulson (*10*), Glasstone (*11*), Sherwin (*12*), Pauling (*13*), Syrkin and Dyatkina (*14*), and Pullman and Pullman (*15*) and to review papers by Coulson (*16*), Longuet-Higgins (*17*), Brown (*18*), and Pullman and Pullman (*19*). Obviously there is too much material and too little time for the student to add much in the line of supplementary material from such a wide variety of texts and papers, but this does ensure that the interested student acquires at least a budding acquaintance with a nucleus of useful literature which may serve as a foundation for future growth.[3]

Incidentally, no real effort is made to get the student to acquire an historical background to quantum mechanics at this time. The writer feels that the historical approach is rather confusing to the beginning student and is best appreciated after gaining some mastery and appreciation of the subject.

It is yet far too early to draw any conclusions about the results of this pedagogic experiment, but a few facts appear to stand out clearly: student interest has been high and the performance on assigned problems has been generally excellent—even in the case of students having a rather scanty background in physics and mathematics, although in many cases it has been necessary to consult quite frequently with such students concerning mathematical and conceptual difficulties. The final examination over the quantum mechanics portion of the course has been an oral quiz of about half an hour. It is truly surprising to find out how much of the outside reading has actually been done (of course, there are the usual exceptions!) and how well many qualitative ideas have caught on.

It should be pointed out that the author makes no claim that the above-outlined course represents the "best" approach to the problem of training organic chemists in quantum mechanics. Teaching is very much an experimental science as well as an art, and it would be indeed surprising if future experiments did not force quite extensive modifications.

In conclusion it is suggested that such a course be taught as part of an advanced physical chemistry course required of all Ph.D. candidates or, possibly, a better arrangement would be as part of a course in theoretical organic chemistry normally required of organic majors.

[3] Recently there has appeared an excellent text by R. Daudel, R. Lefebvre, and C. Moser: "Quantum Chemistry—Methods and Applications," Interscience Publishers, Inc., New York, 1959. This text appeared too late for extensive use in our course, but the author feels that this text is by far the best suited as a single source for the purposes of the outlined course.

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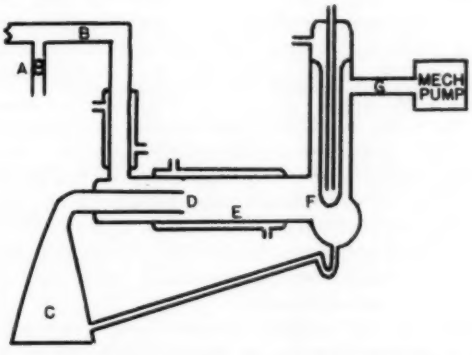
# Demonstration of Evacuation

A frequently-asked question concerns the operation of the mercury diffusion pump which is a common component of many vacuum systems. A visual demonstration of two cycles in the production of a vacuum in a system containing such a pump is described herein. The two cycles correspond to a high and a low pressure range; the mechanical pump alone is operative in the former whereas both the mechanical and diffusion pumps are operative in the latter. The requisite apparatus is shown in the figure.

The particular design of mercury diffusion pump shown is singularly convenient for this demonstration. The room should be darkened to achieve optimum viewing conditions.

The system is evacuated to approximately $10^{-5}$ mm Hg and then exposed to atmosphere by opening and quickly closing stopcock *A*. Consequently the mechanical pump changes sound, and condensation of mercury occurs due to the increase in pressure of the system. A Tesla coil is immediately placed in the vicinity of *C* and the system sparked. Initially a green cloud of newly-evaporated mercury appears over the surface of the heated mercury at *C*. The green color is the 5460 Å line of mercury, electronic excitation being produced by the electrical discharge of the Tesla coil. The green cloud advances randomly upward from *C*. A streamlined, conical-shaped flow pattern is eventually established with base at *D* and apex at *F*. The duration of the pattern is directly proportional to the pumping speed of the mechanical pump. If the pattern is too short-lived, stopcock *A* must be kept open slightly during the demonstration.

The flow pattern described above is observed only in the first cycle, i.e., in the high pressure range where evacuation of the system is due only to the mechanical pump. It should be emphasized that the diffusion pump is not operative in this range; a minimum pressure $\leq 10^{-3}$ mm Hg must be established in the fore system, *G*. Furthermore in this high pressure range no visible condensation of mercury occurs along *E*. The large number of air molecules rushing through the diffusion pump confine the mercury atoms to the conical-shaped pattern. Mercury does not condense along *E* but solely at *F*.




As the pressure of the system is further diminished the flow pattern disappears, and condensation of mercury occurs along *E* rather than at *F*. The second cycle is now initiated and diffusion of mercury atoms at *D* occurs. The diffusion process leads to pressures in the back system, *B*, less than those obtainable with the mechanical pump alone. Due to the reduced number of air molecules in the system, the high velocity mercury atoms existing at *D* are no longer confined to a flow pattern. Velocity energy is imparted to air molecules from *B* by collision with the mercury atoms. Air molecules are thus "kicked" over into *G* and swept away by the mechanical pump. In order to minimize backward flow into *B*, the mercury atoms must be quickly condensed, a feature first recognized by I. Langmuir. In this type of diffusion pump such condensation occurs mainly along *E*.

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# Growth and Decay of Radionuclides

## *A demonstration*

Laboratory exercises in radioactive decay can be conveniently carried out with many different radionuclides. If multiple laboratory sessions are available, radionuclides having half lives of several days or more can be used (*1*). On the other hand, if the exercise is to be completed in one session, it is desirable to use nuclides having half lives in the range of hours (*2*, *3*), or better still, minutes. Use of the latter provides a dramatic demonstration and leads to a more accurate half-life determination by the student, since he can easily follow the decay process through a number of half lives during the laboratory session.

The purchase and transport of individual radioisotopes having extremely short half lives is obviously impractical. Activation of various stable isotopes will lead to a number of short-lived radionuclides (*4*, *5*), but neutron sources for activation often are not available. Another approach to the supply problem is the use of a parent-daughter pair. The half life of the parent should be long, and the short-lived daughter should decay to either a stable or long-lived isotope. If some rapid method is available for the separation of the short-lived daughter, an apparatus can then be set up for laboratory production of the daughter as required. The daughter is "milked" from the apparatus containing the parent, and hence the setup is referred to as a "cow."

Of the very short-lived parent-daughter pairs that have been described as laboratory aids for demonstrating radioactive decay, the pair, $Bi^{207}$ ($t_{1/2}$ = 8 yr) — $Pb^{207}$ ($t_{1/2}$ = 0.8 sec), suggested by Jones (*6*), is probably not usable for other than an auditory demonstration of decay, since the half life of the daughter is so short. Special equipment would be required for quantitative measurements.

Booth (*7*) and recently Carswell and Lawrance (*8*) have suggested the use of the parent-daughter pair, $Th^{234}$ ($t_{1/2}$ = 24.1 days) — $Pa^{234}$ ($t_{1/2}$ = 1.18 min). The half life of the parent in this pair is unfortunately rather short. Carswell and Lawrance separate the thorium[234] from natural uranium; protactinium[234] is then separated from thorium[234] by solvent extraction techniques.

The parent-daughter pair, $Ce^{144}$ ($t_{1/2}$ = 285 days) — $Pr^{144}$ ($t_{1/2}$ = 17 min), suggested by Bradley and Adamowicz (*9*), is a better pair for use in laboratory exercises. Even so, the method suggested for daughter separation (precipitation of cerium as the iodate, followed by filtration) is objectionable from the viewpoint of time consumed and potential laboratory contamination, unless techniques in handling radioisotopes are to be stressed.

[1] Under contract with the United States Atomic Energy Commission.

Another parent-daughter pair, $Cs^{137}$ ($t_{1/2}$ = 30 yr) — $Ba^{137m}$ ($t_{1/2}$ = 2.63 min), has a number of advantages over other pairs suggested for laboratory exercises in radioactive decay. The half life of cesium[137] is quite long. Cesium[137] is available and inexpensive in the amounts required for laboratory exercises. In addition, an ion exchange technique can be used for the separation of barium from cesium, and the inconvenience of solvent extraction or precipitation is thus avoided.

Newacheck, *et al.*, (*10*) have reported the design of an ion exchange device that can be used to separate barium[137m] from cesium[137]; however, they give no details on the elution procedure used with their device.

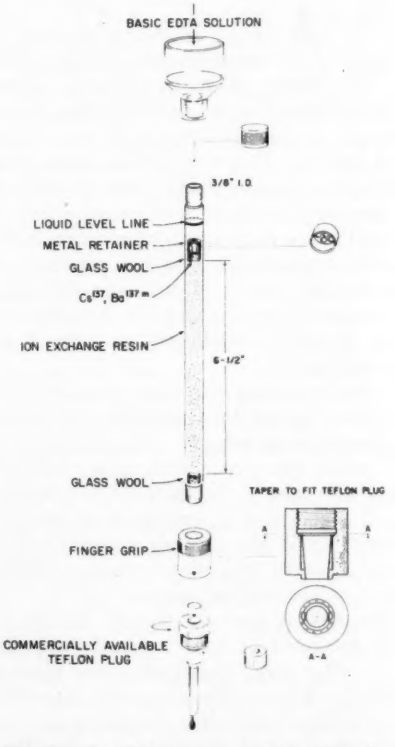


**Figure 1. Diagram of exchange column used for production of $Ba^{137m}$.**

A simple ion exchange technique has been developed at the Medical Division for the separation of $Ba^{137m}$ from $Cs^{137}$ in approximately 30 seconds and in a yield of 80 % of the theoretical. The method as used in our laboratory exercises has been highly successful. Because of the high yield and short separation time, it is also possible for the student to study radionuclide growth, in addition to decay, by measuring the buildup

of barium$^{137m}$ on the column after elution. This demonstration of growth to secular equilibrium can then be related to neutron activation in reactor production of radioisotopes or other processes involving a $(1 - e^{-x})$ relationship. The following is a description of the apparatus and the technique developed for its use in laboratory exercises.

### *Apparatus*

The ion exchange apparatus is shown in Figure 1. It is constructed completely of transparent plastic except for the stopcock plug, which is made of Teflon. The plug indicated is a type that is commercially available under the trade name "Ultramax."[2]

The all-plastic construction was an attempt to make the column as "student proof" as possible. The column can, of course, be fabricated from a buret, but under those circumstances there is always the possibility of accidentally shattering the column and contaminating the working area. If only a few microcuries of cesium$^{137}$ are involved, there would be no immediate physical danger; however, spillage does involve the potential hazard of human ingestion as well as instrument contamination, if the area is not properly cleaned. In the plastic column a glass wool plug and a stainless steel retainer are inserted above the ion exchange resin to prevent loss of active resin should the column be tipped over.

The resin height indicated in Figure 1 was dictated by the height of the assembled column, which in turn was the result of an emphasis on stability and storage convenience. Another resin height can, of course, be used; the data given in the discussion of the method, however, apply only to the dimensions shown in Figure 1. The column is constructed of commercially available plastic tubing.

With the diameter and height of the resin column indicated in Figure 1, a 10-ml portion of eluant is sufficient for stripping the column of the available barium$^{137m}$ activity. If the column is filled with resin (wet mesh 20–50) by gravity, no vacuum is required, and a 10-ml portion of eluant will flow through the column in approximately 30 seconds.

When the column is not in use, the funnel and stopcock tip can be replaced by the caps indicated in Figure 1. The apparatus may then be conveniently stored in a horizontal position.

### *Laboratory Method*

Barium$^{137m}$ can be separated from its cesium$^{137}$ parent by elution from cation-exchange resins of the sulfonic acid type with ethylenediamine tetraacetic acid (EDTA). In arriving at a technique for a laboratory exercise, emphasis was necessarily placed on speed of separation as well as on yield. Another important consideration was the potential cesium$^{137}$ contamination of the barium$^{137m}$ preparation, since cesium$^{137}$ does gradually descend the column.

In initial trials, it was found that the permeability of the exchange resin was an important factor in the yield of barium$^{137m}$. Of the various exchange resins tried, Dowex 50W-X1 (wet mesh 20–50) gave the highest barium$^{137m}$ yield. Of the various forms of Dowex 50W-X1 tried the potassium form gave the best barium$^{137m}$ yield. The difference between various alkali metal forms was not great, however.

The EDTA elution yield of barium$^{137m}$ from the potassium form of Dowex 50W-X1 is constant from a *p*H of 13 down to a *p*H of 10. Below *p*H 10 the yield drops. Above *p*H 11.5 the cesium$^{137}$ tends to spread rapidly down the column with repeated elutions. A compromise *p*H of 11 was consequently adopted for the column.

The yield of barium$^{137m}$ from the potassium form of Dowex 50W-X1 with EDTA eluants at *p*H 11 is constant at about 80% of theoretical for EDTA concentrations from 1% down to 0.05%. Below 0.05% the yield drops rapidly. On the other hand, although the barium$^{137m}$ yield is independent of EDTA concentration in this range, the higher the EDTA concentration used the greater is the mobilization of the cesium$^{137}$ on the exchange column. This behavior is shown in Figure 2. An EDTA concentration of 0.05% was consequently adopted for experiments requiring a maximum elution of barium$^{137m}$.

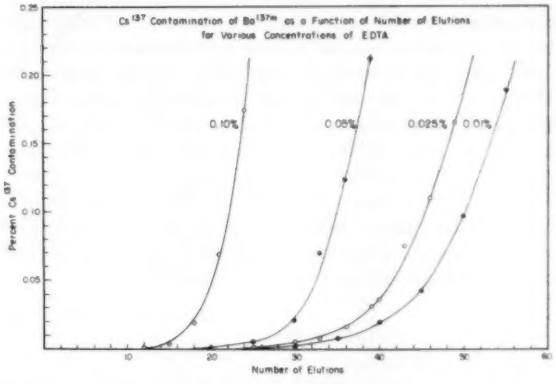


**Figure 2. Cs$^{137}$ contamination of Ba$^{137m}$ preparation as a function of number of elutions for various EDTA concentrations. Resin, Dowex 50W-X1 in potassium form. Eluant *p*H, 11.**

With an EDTA concentration of 0.05% and a resin column of the height and diameter shown in Figure 1, approximately 30 elutions can be made before the cesium$^{137}$ contamination reaches a level of 0.01% of the barium$^{137m}$ yield. Even after the barium$^{137m}$ preparation has decayed through eight half lives, this level of cesium$^{137}$ contamination will introduce an error of only 2.5% in the net counting rate.

The useful life of the cow can of course be greatly extended by increasing the height of the resin column. A larger volume of eluant will then be required. If the yield of barium$^{137m}$ is not important, the useful life can be increased even further by decreasing the EDTA concentration (Fig. 2). The loss in barium$^{137m}$ yield will, however, dictate a limit on the increase in column life by this method. By using such methods the useful life of the cow can be extended to hundreds of elutions.

Our procedure for setting up the cesium$^{137}$ cow is to convert the Dowex 50W-X1 resin to the potassium form, fill the column by gravity, and charge the top of the resin column with cesium$^{137}$ in dilute hydrochloric acid.[3] The column is next flushed with distilled water and then with three 10-ml portions of EDTA eluant.

[2] Fisher and Porter Company, Hatboro, Pennsylvania.

[3] "Processed, carrier-free" from Oak Ridge National Laboratory.

The free acid is used in the preparation of the EDTA eluant; the *p*H is adjusted with potassium hydroxide.

In laboratory exercises with this demonstrator, it is best to use a scintillation detector, if one is available. Wide ranges in counting rates can then be handled without the coincident loss that would occur with a G-M detector. Also, the amount of cesium$^{137}$ required will be at a minimum (a fraction of a microcurie for decay exercises) if a scintillation detector is used.

A counting time of 10 seconds has been adopted for our laboratory exercises. This short interval is used so that the students can accumulate a large number of measurements. The counting period can be of any reasonable length so long as the same period is adhered to during the course of the exercise.

In an experiment to demonstrate radionuclide growth to secular equilibrium, it would be desirable to have as complete a separation of the daughter from the parent as possible. This is the reason emphasis was placed on the maximum yield of barium$^{137m}$ in the development of a laboratory technique for the separation of barium$^{137m}$ from cesium$^{137}$. It is impossible under the circumstances to realize a complete separation, since a finite time is involved in carrying out the operation. However, at the separation levels that have been achieved, the growth process is easily observed by taking a count on the column immediately after the elution and using this count to correct further counts for the initial incompleteness of the separation. A count of the column before elution is assumed to be the secular equilibrium count. Figure 3 shows a typical buildup curve obtained by this procedure.

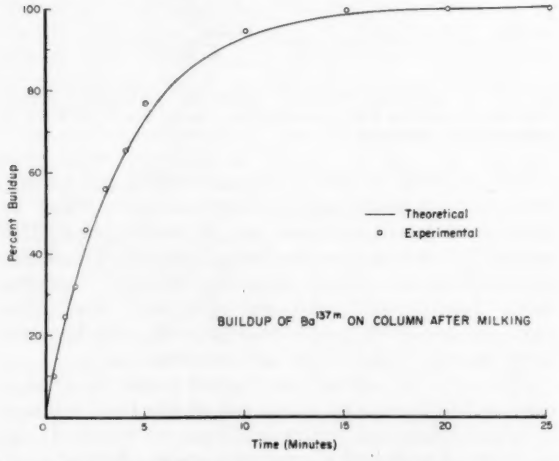


**Figure 3. Growth of Ba$^{137m}$ on exchange column after elution.**

Cesium$^{137}$ decays to barium$^{137m}$ by beta minus emission while barium$^{137m}$ decays to stable barium$^{137}$ through a gamma-ray isomeric transition that is partially converted. Most of the electrons associated with these decay processes are stopped by $^1/_8$ in. of plastic, the wall thickness used in our plastic exchange column; some particles are, however, energetic enough to traverse this thickness. In our laboratory exercise, these energetic electrons are absorbed by the covering over the detector. If an end-window GM-tube is used as the detector in an exercise to demonstrate radionuclide growth, it may be necessary to add additional shielding on the column or over the detector to avoid an excessive counting rate for the zero time correction.

A typical plot of barium$^{137m}$ decay is shown in Figure 4. In our experience students have usually obtained a half-life value within 0.1 min of the reported half life, 2.60 and 2.63 min (*11*). This is quite gratifying for both student and instructor.

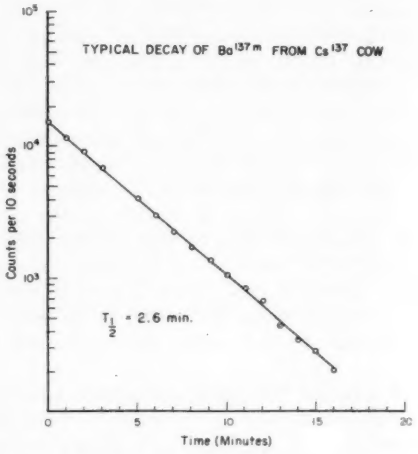


**Figure 4. Typical plot of Ba$^{137m}$ decay.**

## Summary

A simple and rapid laboratory method for the separation of barium$^{137m}$ from cesium$^{137}$ has been developed. The technique may be used for laboratory exercises or for lecture demonstrations to show radionuclide growth to secular equilibrium as well as radionuclide decay. Since the half life of barium$^{137m}$ ($t_{1/2}$ = 2.63 min) is conveniently short, both processes can be easily demonstrated in one laboratory or lecture period.

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# A Technique for Packing Columns for Gas Chromatography

The problem of packing columns for use in gas chromatography can become a tedious and time-consuming one when the operation is performed manually. In order to eliminate this difficulty, a simple device has been designed which is easily constructed from readily-procured pieces of apparatus and which provides for packing either a single column or two columns simultaneously.

In Figure 1 the following parts are identified. Part A is the motor and shaft of a record player mounted vertically on angle irons which are fastened to the seat of a laboratory stool. Part B is a thin metal disc, 6 in. in diameter, mounted on the shaft of the motor. A similar disc is mounted opposite this one and is connected by a 2-in. shaft, $1^1/_2$ in. off center. This shaft has on it a wooden spool from a spool of sewing thread. The metal rod of the shaft is small enough so that the spool easily rolls when the disc is rotated. Mounted on the outside edge of the second disc and 180° from the position of the spool is a $2^1/_2$-in. length of bar solder, indicated as part C in the picture. Part D is a 45-in. piece of $^1/_2$-in. copper tubing, which has a $2^1/_2$-in. side arm of the same tubing welded at 90° and in a position 32 in. from the lower end. This tube has a rubber covering at the base for the purpose of absorbing some of the sound. Two small ring clamps guide the jacket, one mounted on the lowest rung of the stool about 6 in. above the floor, and the second on the top of the stool, 24 in. above the floor. Inside this tube is placed the 4-ft.-long, $^1/_4$-in. tube which has previously been plugged at the lower end with a wad of glass wool. A small plastic funnel is fastened to the upper end with a piece of rubber tubing.

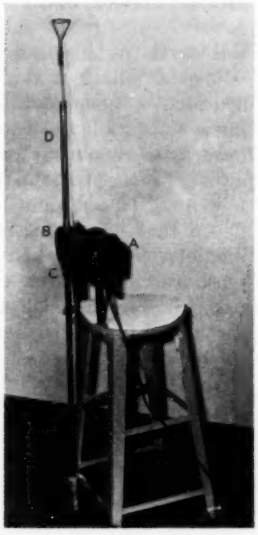


Figure 1. Apparatus designed for filling single column: A, motor; B, disc; C, bar solder; D, jacket.

When the motor is started, the disc rotates, lifting up the jacket and column and raising them about 3 in. above the floor. The rate of lifting is 78 times per minute. The spool carrying the jacket rolls under the side arm until it reaches the end, causing the jacket and its contents to drop to the floor. The heavy load which is being lifted is counterbalanced by the piece of bar solder mounted opposite the spool. The only manual work necessary is periodically to add the substance which is being used to fill the column.

The apparatus is modified slightly in such cases where it is desirable to fill two columns simultaneously. In Figure 2 the leverage system is made of $^1/_2$-in. strap iron and mounted to a second jacket, similar to the one described above. As the spool makes its path downward, it depresses lever E, raising the jacket. As the spool rolls off this lever, the jacket will drop to the floor giving the same type of motion as was accomplished in the other jacket.

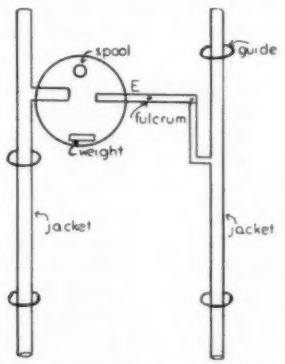


Figure 2. Apparatus designed for filling two columns simultaneously E, lever arm.

A comparison was made between the columns which were filled manually and those which were filled by means of this technique. In both cases the flow rate of helium through the columns was the same for the same external pressure of the gas. The efficiency of the columns was also identical.

Since this problem of packing columns can be a noticeable variable when the packing is done by more than one individual, this piece of apparatus has been of advantage both in achieving uniformity in packing and in saving time.

Acknowledgment is due to John H. Ven Horst for his assistance in constructing the apparatus.

## Erratum

The price of MCA's "Matter, Energy and Change" as quoted on page 445 of the September issue is in error. It should read "72 cents per copy, no discount on quantity order."
Write Holt, Rinehart and Winston, Inc., 383 Madison Ave., New York 17, N. Y.

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# Drugs Used by Paracelsus

## *A brief survey*

Paracelsus, known to many chemists by his given name Theophrastus Bombastus von Hohenheim, (1493–1541) is lauded as the father of modern pharmacy (*1*). Many chemists will not agree that the roots of modern pharmacy reach this far back into history. However, Paracelsus certainly was instrumental in changing the approach to drug treatment because he did use specific chemical substances—both inorganic (i.e., minerals) and organic (herbs).

Since he lived during the period of the Renaissance, to say that Paracelsus used drugs would imply that he was an apothecary. But a man who made the following scathing criticism of the apothecaries of his day would not welcome such a designation (*2*):

> The apothecaries are my enemies because I will not empty their boxes. My recipes are simple and do not call for forty or fifty ingredients.

That Paracelsus spent most of his lifetime wandering from place to place is a well-established fact. It is doubtful, then, that he had a specific place to prepare his prescriptions. If he did, however, the shingle would probably have read: Theophrastus Paracelsus, Chemist. It is said that "wherever he stopped on his pilgrimage, he brewed his drugs on the charcoal under the chimney, right beside the hostess' soup." (*3*) His vessels were simple and typical of those found in every alchemist's supply room—a pelican (i.e., a retort or still), a mortar and pestle, a crucible, and an alembic.

Paracelsus, in somewhat mystical language, summed up his philosophy for the preparation of drugs in the following statement (*4*):

> God created iron but not that which is to be made of it. He enjoined fire, and Vulcan, who is the lord of fire, to do the rest . . . Iron must be cleansed of its dross before it can be forged. This process is alchemy; its founder is the smith Vulcan. What is accomplished by fire is alchemy—whether in the furnace or in the kitchen stove. And he who governs fire is Vulcan, even if he be a cook or a man who tends the stove. The same is true of medicine. It too was created by God but not in its finished state, but still concealed in dross . . . What the eyes perceive in herbs or stones or trees is not yet a remedy: the eyes see only the dross. But inside, under the dross, there the remedy lies hidden. First it must be cleansed from the dross, then it is there. This is alchemy, and this is the office of Vulcan; he is the apothecary and chemist of the medicine.

Some of the so-called simple remedies of Paracelsus would have little consumer-appeal on the shelves of a modern druggist. The oil of hard-boiled eggs was a necessary but ill-smelling ingredient in many preparations. A drug called *Confectio Antiepileptica* was made by distillation from the skull of a man never buried (*5*). (Drugs of this type were referred to as *mumia*.) A basic ingredient of many remedies was a distillation of herbs which had been putrefied for a month or more (*6*). It is apparent, then, that Paracelsus believed that remedies should be separated (or extracted) from vegetable or animal matter. This was in opposition to the apothecaries who believed that drugs should be compounded.

Although Paracelsus employed vegetable and animal products, he was best known for the use of mineral products. At about the age of nine—in 1502—Paracelsus was taken by his father, a physician, to the mining village of Villach, and as he grew to manhood there he acquired a first-hand knowledge of the mines. He knew the problems of extracting the minerals and the hazards to which the workmen were exposed. He was aware of the poisonous effects of arsenic, mercury (*argentum vivum*), and lead on the workmen. He believed that lung diseases were possibly caused by the inhalation of this dust. Later, he used these same poisonous substances—arsenic, mercury, lead—in his practice. In his own day, Paracelsus was famous for the use of poisons and the detoxification of poisonous substances. He reasoned accurately that if poisons were used sparingly they were of use in the treatment of disease. Poisons do figure prominently in the so-called pharmacoepia of Paracelsus.

Paracelsus used mercury externally in the treatment of cutaneous diseases, following the tradition of Arabian doctors, and internally to promote diuresis and as a purgative (*7*). He gained his greatest fame in the use of mercury, however, by using it as a cure for syphilis, or as he calls it, the French disease (*1*). The use of mercurial compounds, especially in the treatment of dropsy, is discussed under Sulfur, Salt, and Mercury.

Arsenic was employed to treat skin diseases, antimony and arsenic in the treatment of cancer and leprosy (*6*). As stated in the Third Defense of Paracelsus (*8*):

> Though a thing is poison, it may well be turned into a non-poison. Take an example from Arsenic . . . burn it with *Sal nitri* and it is no longer poison. Eating ten pounds is harmless.

It will simplify the use of terms if we first identify Salt, Sulfur, and Mercury as the three principles of Paracelsus, and then investigate the chemical substances which Paracelsus called salt, sulfur, and mercury.

Paracelsus believed that all bodies were composed of the three principles—Salt, Mercury, and Sulfur. The example of a piece of burning wood is often used to illustrate these principles: The flame corresponds to the Sulfur (i.e., that which burns and is consumed);

Presented before the Division of History of Chemistry at the 136th Meeting of the American Chemical Society, Atlantic City, N. J., September, 1959.

the smoke to the Mercury (that which fumes and disappears in vapors); the solid ash remaining, to the Salt. The three principles are not the same in each remedy—they differ in quality.

> A different Sulfur is found in gold, another in silver, another in iron, lead, zinc, and so forth—the same is true of Salt and Mercury. They are still more divided, so that there is not only one kind of gold, but many kinds of gold, just as there is not only one kind of pear or apple but many kinds. Therefore, there are just as many different kinds of Sulfurs of gold, Salts of gold, Mercuries of gold (*9*).

Paracelsus was familiar with salt mines firsthand and knew that the workers in these mines were not exposed to the same dangers as the mineral workers. A salt was recommended as a cure in the treatment of goiter (*10*); the salt vitriol could cure one-fourth of all diseases, even leprosy (*8*).

In the treatment of dropsy, "mercurial essences"—probably mercurial oxide—were of value in removing a large accumulation of water from the patient's body. Sulfur and a metallic "crocus" (oxide) were administered; the sulfur was supposed to act as a sun dispelling the rain in the microcosm (i.e., man), while the metallic crocus would dry the body of the patient (*11*). Paracelsus observed that sulfur derived from vitriols and salts was stupefactive, narcotic, analgesic, and hypnotic. In its natural condition it was sweet and caused a deep and harmless sleep in chickens (*10*). (It has been suggested that Paracelsus anticipated the modern method of testing drugs on animals.)

What are today termed mental illnesses were also treated by Paracelsus. He referred to the maladies, including epilepsy, as "Diseases That Deprive Man of His Reason." He observed:

> Against material diseases material remedies should be applied; against spiritual diseases, spiritual remedies. There are some material remedies which cure spiritual diseases (*12*).

Paracelsus believed that medicine was found not only in herbs, wood, and stones but also in words; "As the disease is, so is the medicine (*8*)."

The seven metals of ancient times, allied so closely with the seven planets, are included in the list of Paracelsean drugs. These "drugs" were available in the following forms:

Gold: colloidal and chloride
Silver: colloidal, nitrate, and possibly chloride
Mercury: nitrate, and possibly chlorides
Iron: nitrates, sulfates, and chlorides
Copper: nitrates, sulfates, and chlorides
Lead: nitrate and chlorides
Tin: nitrate, stannous chloride, and possibly stannic chloride.

Of these seven metals, it is of interest to note that the nitrates of all but gold are included and probably the chlorides of all the metals. Gold and silver are both included in the colloidal state.

According to Multhauf, the minerals most frequently mentioned by Paracelsus were vitriol, gold, antimony, and mercury. He also used bismuth (called white marcasite) and nickel fairly often. A few of the compounds of these minerals which deserve mention are sodium and potassium sulfates—known to the followers of Paracelsus by the more familiar names of mirabilite and arcanite, and the acids: metastannic, muriatic, sulfuric, nitric, and aqua regia.

Paracelsus treated some skin diseases with zinc oxide and zinc sulfate. These compounds deserve special mention because they are still effectively used and remain in the pharmacopeia today.

In order to have an understanding of Paracelsean medicine, it is necessary to have some insight into the notions of correspondences and the microcosm-macrocosm idea of Paracelsus. Not only were the seven ancient metals chemical substances; more importantly they played a role in treatment because of the relationship to the planets which governed the celestial element outside man and its equivalent in man. The macrocosm was the natural world—the planets, minerals, animals, and plants. Man was the microcosm. In other words, the sun in the heavens had its counter-part in the earth—gold. It was the sun of the "planetary" world that represented and governed the heart of man.

Such statements as the following, then, do not seem too far-fetched:

> Everything that regenerates is closely related to the heart, such as gold, the balm Melissa, a rose-colored manna called "nuba," and other substances (*10*).

Nor is an investigation of Paracelsean drugs complete without mention of Arcana. Arcana were referred to as compound remedies, secret remedies, or specific drugs directed toward the treatment of individual diseases. Paracelsus obviously did not use the exacting terminology of the twentieth century, for arcanum also meant the "active principle" of a drug (*13*). Certain diseases could not be cured by the usual prescriptions but required the great arcana such as laudanum or pearl remedies. Another arcanum, the tincture of powdered red coral, was helpful to the red blood of the human system (*1*). Other authors mention calomel (mercurous chloride), blue vitriol, and several compounds of zinc, arsenic, and lead. Urdang, however, doubts that calomel was used by Paracelsus (*10*). Sigerist (*13*) believes that Paracelsus gave his prescription for laudanum in his lectures on therapeutics and pathology at Basel during the winter of 1527–28. Multhauf observes that laudanum, derivatives of vitriol, and tartar are the most frequently mentioned remedies of Paracelsus.

Among the vegetable products that he employed the following are worth noting, for they were used in the treatment of mercury poisoning: pepper oil, juniper juices, boiled fresh fir cones and lily of the valley.

Paracelsus employed a wide variety of animal products in treating human ills. For example, oil in which live toads had been cooked healed white and black so-called "leprosy" in plague, and also venomous bites. Field mice could be cooked and used in this same way against consumption, and crabs against cancer (*10*). A healing salve was made by boiling milk with crayfish (*8*). A scorpion's venom cured scorpion poisoning; this is an illustration of the "like-to-like" or homoeopathic principle.

Paracelsus described a great variety of pearl remedies too. The pearls were ground or calcined, mixed with vinegar, alcohol or other substances, and used in many combinations.

Paracelsus is often hailed as an army physician. This further makes him interesting to our generation. Just as methods of warfare have so decidedly changed,

so has the treatment of battle wounds. Apparently, he felt it more advantageous to treat the weapon than the wound. "Weapon salve" consisted of a hodgepodge of remedies that were best smeared on the weapon—be it knife blade or sword—to speed the recovery of the soldier. It was indeed fortunate for the fighting man that the salve was not applied to his cleansed wound. Paracelsus himself has been portrayed with sword in hand, and it is said that in the helm of that sword he carried his very special arcana: laudanum or perhaps red mercuric oxide.

Paracelsus differed from the ancients who knew of only one disease—"distemper"—an upset of the humoral balance. To the forerunners of Paracelsus, therapy consisted of "withdrawing what was in excess" or "adding what was lacking." Remedies, notably herbs, were examined for qualities which would in a sense add to or subtract from the patient.

In the evaluation of Paracelsus as a modern pharmacist it is necessary to review his attitude toward miracle drugs and the belief that a specific drug would be found for each disease. As stated by Paracelsus (*4*):

> In medicine we should never lose heart, and never despair. For each ill there is a remedy that combats it. Thus there is no disease that is inevitably mortal. All diseases can be cured without exception.

If certain remedies of Paracelsus were found to be efficacious, would it be possible to duplicate the prescriptions? Authors disagree on this. Dobler (*10*), for example, was able to duplicate tartar emetic as prepared by Paracelsus. Other authors, however, feel that there are many drawbacks to a duplication of Paracelsean drugs: the evasiveness of the language and sometimes apparent omissions, the purity of our present-day drugs and vessels, and the preciseness of measurement.

J. C. Dalton gave the following recipe from the *De Quinta Essentia* (*14*):

> Take pure gold, reduced to the smallest grains and rubbed to a powder with plumbago. Add to this of the best white wine that can be procured, 100 parts; and white resin of the pine, 10 parts and macerate as before. Repeat this a third time. Then take all the wine from the three successive macerations, place it in a glass vessel, well covered and distill with a strong fire, so that it may come over rapidly. When the distillation is complete, place the liquid in a glass vessel, well covered with a blind alembic, upon a bed of ashes hot enough to burn the hand. Keep it in this condition until 9 parts of the liquor are consumed or dried up, and only the 10th part remains. To this remaining liquid add an equal quantity of the white of egg, shake the mixture and distill slowly and a white liquid will come over which should be set aside. Then increase the heat till the vessel is redhot, when there will come over a material of thin, honey-like appearance and a strong odor. Keep this, for it is the fifth essence of gold and a royal medicine.

In 1873 Dalton commented that he had on the highest chemical authority that the result of this process would be only ammoniacal and empyreumatic substances from the destructive distillation of albumen and some ingredients of wine; it would contain no gold. A sharp critic, Dalton contended that Paracelsus used all remedies indiscriminately and without much caution or intelligence. It cannot be denied that Paracelsus replaced mild remedies with harsher ones.

Paracelsus was a contradictory figure during his lifetime; historically the controversy continues. Karl Sudhoff, who is capable of judging the man Paracelsus, observed: "Many of his doctrines are intelligible to us only now, in the light of our modern experimental medicine (*15*)."

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## New Cumulative Index for Journal of Chemical Education

Copy is now in the hands of the printer for a cumulative index to cover Volumes **26** through **35** (1949 through 1958). A grant from the National Science Foundation has underwritten the preparation of this index. It will be available early in January at a probable price of **$2.50** per copy. Over 9000 entries will appear in the Subject Index; this far exceeds the number of titles and suggests the great potential usefulness of the compilation. This new volume, coupled with the 25 year Cumulative Index covering the years 1923–1948, will greatly enhance the usefulness of the Journal of Chemical Education in its role as "The Living Textbook of Chemistry."

*Proceedings of the*

**California Association of Chemistry Teachers**

**Albert O. Dekker**
Aerojet-General Corporation
Sacramento, California

# Solid Propellants

Solid-propellant rockets are probably the oldest of all modern weapons. The Chinese used rockets several centuries B.C. in warfare (*1*). By 1300 A.D. they began to be used in Europe on the basis of knowledge obtained from the Orient (*2*). However, by 1500 A.D. rockets were displaced by the more accurate cannon except in fireworks and signals. In India, about 1790–1800, native troops used rockets against the British and thus stimulated their interest. In the period 1805–13 the British used rockets developed by Sir William Congreve in various actions of the Napoleonic Wars at Boulogne, Copenhagen, Danzig, and Leipzig. Rockets were used against the United States in the War of 1812 not only at the Battle of Bladensburg, which resulted in the burning of Washington, but also at Baltimore as described in our National Anthem. Rocket units were organized in several European armies, and in the United States in 1846–47 there were 11 rocket batteries organized. William Hale developed a finned spinning rocket of which 2000 were used in landing near Vera Cruz and in the storming of Chapultepec. However, after 1850 rockets went out of use because rifled artillery guns were much more accurate.

The revival of interest in rockets began a little over 40 years ago. In the United States in 1918 Dr. R. H. Goddard of the Smithsonian Institution undertook the development of artillery rockets. Working with a physics student, C. N. Hickman, he made test firings and worked on a plane-to-plane rocket. Interest in the project was not great and it was dropped. Dr. Goddard who continued his work privately is known as the father of modern American rocketry. About 1933 Germany secretly started the development of military rockets, and a little later secret government-sponsored work was started in England and apparently in Russia. In the United States work was done primarily by amateurs. For example, Col. Leslie A. Skinner, who later invented the Bazooka, did experiments on his own. In 1939, Dr. Theodore von Karman at the California Institute of Technology began work for the Army on rockets for jet-assisted take-off of planes. This work eventually resulted in the founding of Aerojet-General Corporation to manufacture the units. In June, 1940, Dr. C. N. Hickman, who was the physics student of Dr. Goddard's in 1918, was now with the Bell Telephone Laboratories and wrote the President of the National Academy of Science emphasizing the military advantages of rockets. A National Defense Research Committee section was set up under direction of Hickman and firing tests were started in September. In this same year, cooperation with the British who supplied their more advanced technical information helped the United States catch up. During the war many different rocket weapons were developed which proved to be extremely valuable both in the European and the Pacific theaters. In the period since the war, effort was first concentrated on the application of rockets to guided missiles and more recently on the application to ballistic missiles and the exploration of space.

Based on a talk given to the Sacramento Section of the American Chemical Society on March 17, 1959.

## Composition of Solid Propellants

Any piece of solid propellant used in a gun or rocket is referred to as a grain. The diameter of a grain ranges from a fraction of a millimeter to several feet. The minimum requirements for any material to be considered as a solid propellant are that the material be capable of fabrication into a grain which will hold its shape, and that the material evolve gas in an exothermic reaction on command. These requirements are met by a special class of plastics which are combinations of oxidizing and reducing agents.

The required mechanical properties are best achieved, though perhaps not necessarily, by plastics because they have structures which permit the achievement of a wide range of mechanical properties. The three types of polymer structures, all of which have been used in making propellants, are the linear amorphous, linear polycrystalline, and crosslinked. The linear amorphous polymers are simply made up of long chain molecules. The polycrystalline polymers are also made up of molecules in the form of long chains but there are regions along these chains which are aligned with similar regions in adjoining chains. The crosslinked polymers can be considered to be made up of long-chain molecules which are occasionally joined together by chemical bonds. The linkages formed in the polycrystalline and crosslinked polymers give them excellent dimensional stability and prevent deformation or flow at elevated temperatures. An example of a propellant based on a linear amorphous polymer is the asphalt propellant ALT-161 used in the original Aerojet-General JATO. A propellant based on a polycrystalline polymer is double-base powder, which contains nitrocellulose. Propellants based on crosslinked polymers are the vinylpolyester propellants, hydrocarbon rubber propellants, polysulfide propellants, and polyurethane propellants.

All these polymers used as binders in solid propellants are essentially reducing agents with the exception of nitrocellulose. It is necessary to mix them with oxidizing agents in order to obtain propellants.

The gas and heat generation required of a solid propellant are usually achieved by a mixture of oxidizing and reducing agents which react to give approximately 3 to 5 moles of gas/100 g and 600 to 1300 cal/g or 1100 to 2300 Btu/lb of propellant. The oxidizing agent is usually a crystalline inorganic salt (usually potassium or ammonium nitrate or perchlorate) or one or more organic nitrates or nitro compounds. The reducing agents are usually compounds of carbon such as those with hydrogen, sulfur, nitrogen, and even oxygen. Carbon itself is also used as a reducing agent and considerable work is now being done with aluminum, magnesium, and boron. However, it is almost always necessary to have part of the reducing agent present as a polymer in order to obtain satisfactory mechanical properties. Nitrocellulose contains both oxidizing and reducing agents in the same molecule.

### Specific Solid Propellants and Processes

The two classes of solid propellants used in rockets are double-base powder and composite propellants. Each class can be produced by three well-defined processes; extrusion, compression molding, and casting. In the sections which follow, selected propellants and their processes will be described.

*Double-base propellant* consisting of the polycrystalline polymer nitrocellulose plasticized with nitroglycerin was the first modern solid propellant for rockets. It was first prepared for gun use in the period between 1885 and 1890 shortly after the successful French development of single-base propellant which consists simply of nitrocellulose.

Table 1 gives the composition of a typical double-base propellant (*3*). The flame temperature of this propellant in a rocket operating at constant pressure is 2930°C. Nitroglycerin, the original plasticizer, was replaced in large part by diethylene glycol dinitrate by Germany during the period between World Wars I and II in order to avoid shortages of ammunition due to shortages of the fats from which glycerin was manufactured. The polymer on which double-base propellant is based is nitrocellulose. If all the hydroxyl groups in each glucose unit are replaced with nitrate groups, the nitrocellulose has a nitrogen content of 14.1%. Actually, propellants are prepared from nitrocellulose containing only 12 to 13.2% nitrogen and, therefore, some of the hydroxyl groups in the long chain composing the molecules have not been nitrated. The degree of nitration and the molecular weight of the cellulose greatly affect not only the processing behavior of the material but also the mechanical properties of the propellant.

Double-base propellant was originally formed into grains by extrusion which is facilitated either by use of a solvent, which is later removed, or with certain compositions by heating to temperatures of from 45 to 60°C. In the former the softening is a result of dissolving the crystalline regions and in the latter a result of melting the crystalline regions of the molecules. Solvent extrusion is limited to the fabrication of grains in which the web thickness is one inch or less because of the time required to remove the solvent. The Bazooka rocket employed a charge of this type. Dry extrusion has been applied mostly to charges one to five inches in diameter. The equipment is massive and expensive but it was the source of most of the rocket propellant, except for Bazooka propellant, used in World War II by the United States. Prior to dry extrusion the propellant ingredients are mixed with water to give a slurry resembling a non-sticky cooked cereal. The water is removed by filtration and subsequent rolling on a heated two-roll mill. Much of the data obtained during World War II on extruded propellant has been published in the open literature (*3*). An elementary book covering the general field of rocket propellants is also available (*4*) which covers double-base propellant very well. For example, it gives the composition and methods for a casting process used for double-base propellant.

*Composite propellants*, consisting of a crystalline oxidizer imbedded in a fuel binder, are also produced by a variety of processes but the most important is casting. Table 2 shows the composition of a representative composite propellant.

**Table 1**

| Material | Wt. % | Purpose |
|---|---|---|
| Nitrocellulose (13.25% *N*) | 51.5 | Polymer |
| Nitroglycerin | 43.0 | Explosive plasticizer |
| Diethyl phthalate | 3.25 | Non-explosive plasticizer |
| Ethyl centralite | 1.0 | Stabilizer |
| Potassium sulfate | 1.25 | Flash suppressor |
| Carbon black (added) | 0.2 | Opacifying agent |
| Candelilla wax (added) | 0.08 | Die lubricant |

**Table 2**

| Material | Wt. % | Purpose |
|---|---|---|
| Ammonium perchlorate | 75.0 | Oxidizer |
| Polymer | 22.0 | Fuel, binder |
| Additives | 3.0 | Curing catalyst<br>Burning-rate accelerator<br>Processing aids |

The oxidizers available are relatively few in number compared to the fuels available. Table 3 shows the most important oxidizers, their percentage of available oxygen, densities, heats of formation, and moles of gas contributed per 100 g in the exhaust when incorporated in a propellant formulated from carbon, hydrogen, oxygen, chlorine, and nitrogen compounds. Potassium and lithium perchlorate are not considered to contribute to the number of moles of gas formed as their oxygen enters into molecules of carbon monoxide or hydrogen from the binder.

It is desirable for an oxidizer to have a high oxygen content and density, produce a large number of moles

**Table 3. Oxidizers for Solids Propellants**

| | Available wt. % $O_2$ | Density lb/in.$^3$ | Heat of formation kcal/100 g | Moles of gas/100 g |
|---|---|---|---|---|
| $KClO_4$ | 46.0 | 0.090 | −82 | 0 |
| $KNO_3$ | 39.5 | 0.076 | −118 | 0.495 |
| $NH_4ClO_4$ | 34.0 | 0.070 | −59 | 2.55 |
| $NH_4NO_3$ | 20.0 | 0.061 | −110 | 3.75 |
| $LiClO_4$ | 60.0 | 0.087 | −86.5 | 0 |

of gas, and have a low heat of formation (i.e., evolve little or no heat when formed from the elements so that the reaction will be more exothermic when the oxidizer reacts with the fuel). It is interesting to note that the best oxidizer cannot be picked by simply examining the data in this table. Detailed thermodynamic calculations or measurements of performance in rockets are necessary. These show that ammonium perchlorate and lithium perchlorate give the highest performances followed by ammonium nitrate.

The fuel binders evaluated in the past have included virtually all the natural and synthetic polymers: for example, vinylpolyesters, polysulfides, polyurethanes, and nitrocellulose. Most of them have densities of the order of 0.035–0.05 lb/in.$^3$ and it would be desirable to increase this. It is desirable that they contain as much hydrogen as possible in order to increase the number of moles of gas evolved on combustion. It would also be desirable for them to contain elements or linkages which evolve more energy when reacting with the oxidizer.

Composite propellants have been outstanding for the fact that they can be poured or cast into the rocket motor and thus do not require the use of extrusion presses. As a consequence the fuel binder is characteristically low in viscosity during mixing and casting and then requires a curing step in which the viscosity is greatly increased in order to form the solid propellant grain. With asphalt binder the two viscosity ranges were achieved by first heating the propellant during the mixing and casting step and then cooling to form the grain. With modern propellants the low viscosity is often achieved by use of relatively low molecular weight liquids which do not react significantly during mixing and casting but polymerize on heating.

Polyurethane rubber is a good example of a binder for composite propellants. In its simplest form the binder is based on a diisocyanate and a long-chain diol. The polymerization reaction forms linear molecules but crosslinking is introduced by the use of a compound containing three hydroxyl groups (a triol). In this way a three-dimensional network is built up. The structures of the diisocyanate, diol, and triol may be varied to produce differences in the mechanical properties and processing characteristics of the propellants.

### Mechanical Properties of Solid Propellants

The methods of mounting solid-propellant grains in chambers determine in part the mechanical properties which are required for the propellant. These methods are of two main types, one in which the grain is held in place by traps at the ends and the other in which the grain is bonded to the chamber wall either with or without an insulating liner between. The propellant must have a sufficiently high modulus to prevent gross deformation of the grain under operating conditions On the other hand, the propellant must have a sufficiently low modulus to enable it to accept a certain amount of deformation without cracking which would increase the propellant burning area and possibly rupture the chamber. Any temperature change produces a thermal expansion or contraction, an unavoidable strain. Because the presence of these strains is inevitable, the binders for solid propellants are usually compounded from rubbery materials which retain their rubber-like properties at very low temperatures.

### Ballistic Properties of Solid Propellants

This section will consider the behavior of a rocket propellant during combustion in the motor and the factors which determine the performance of a rocket (*1*).

Burning of solid propellants occurs in the simplest possible way. Like a cigaret, the burning surface moves in a direction normal to the surface itself. The speed of burning, which depends on the composition, is of the order of 0.25–1.0 in./sec at 1000 psia and 25°C for many propellants. The burning rate usually increases with temperature by the order of 0.2–0.4%/°C The dependence upon pressure can often be described by the equation

$$r = cp^n \qquad (1)$$

in which $r$ is the burning rate, $p$ is the pressure, and $c$ and $n$ are constants. Theory shows that a rocket cannot operate unless $n$ is less than one. This can be understood from Figure 1 in which are shown two possible cases for the value of the pressure exponent.

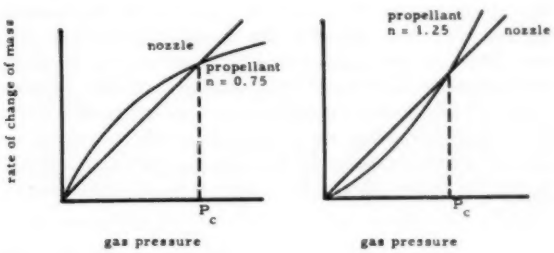


Figure 1.

In this figure are plotted the separate effects of pressure on the mass rate of flow of gas through the nozzle and the mass rate of production of gas by burning the propellant. The burning propellant produces gas at a rate which is proportional to some power of the pressure, $n$, while the nozzle vents the gas at a rate proportional to the first power of the pressure. At a certain chamber pressure, $P_c$, these rates will be equal. A disturbance in which the chamber pressure rises or falls momentarily is automatically corrected in the first case, for which $n$ is 0.75, but in the second, for which $n$ is 1.25, leads to still larger and ever increasing pressure which bursts the chamber. Experience shows that satisfactory motors have been developed for propellants with values of about 0.75 or less. High values make the chamber pressure susceptible to larger variations and make heavier chambers necessary. Naturally, a good deal of research and development work is directed toward obtaining the lowest possible temperature and pressure dependence of the burning rate.

Now, let us look at the fundamentals of rocket operation and thus learn the important factors which determine rocket performance. The fundamental principle of the operation of a rocket is extremely simple. Probably a rocket motor is the simplest of all motors. A rocket is a rigid container for matter and energy so

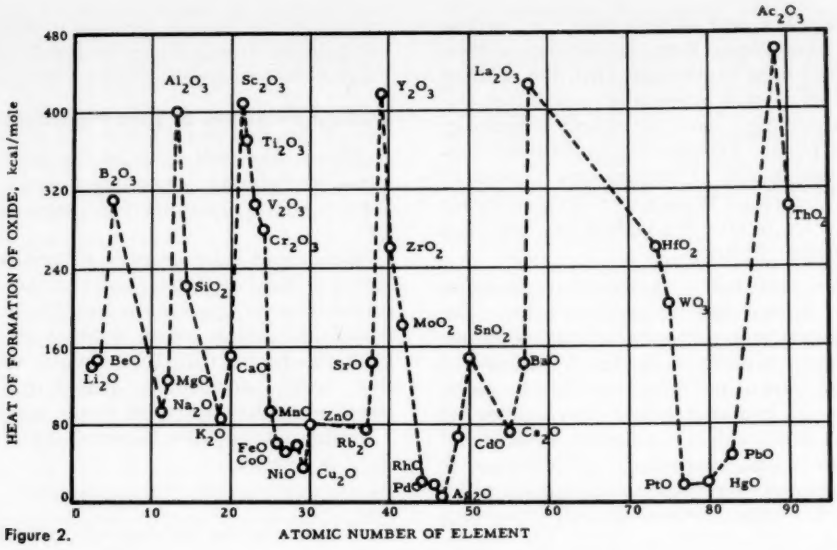


Figure 2.

arranged that a portion of the matter can absorb the energy in kinetic form and be ejected in a specified direction. Inside a rocket motor the burning gases exert a force on each square inch equal to the pressure, $P_c$, of the gas in the chamber. Except for the surface of the chamber opposite the nozzle throat area, $A_t$, the force on any square inch is balanced by an equal and opposite force on the opposite side of the chamber. Thus, the force moving the rocket forward is apparently $P_cA_t$ but this must be corrected for the effect of the nozzle which expands the exhaust gas adiabatically and converts more thermal energy into kinetic energy. Therefore

$$F = C_fP_cA_t \tag{2}$$

where $C_f$ is the nozzle thrust coefficient, usually of the order of 1.5.

What properties are used to characterize the performance of a rocket? For a rocket used for assisted takeoff of planes the emphasis is on delivering a certain required thrust for a certain time. The product of thrust and time is called impulse. However, for rockets fired at moving targets or used in launching satellites or space vehicles the emphasis is on imparting a high velocity $v_b$ to a vehicle of mass $m_b$ by the time the propellant has burned out. The product of mass and velocity is called momentum. Actually, impulse and momentum are dimensionally equivalent as we see from the following equation:

$$Ft = \text{mass} \times \text{length} \times (\text{time})^{-1} = m_bv_b \tag{3}$$

Thus, for a rocket, impulse and momentum change are significant rather than energy dissipated or power generated.

Having considered the quantities which are important for a rocket motor, let us consider those for the rocket propellant. The impulse per unit weight of propellant or the thrust per unit weight-rate of flow is called the

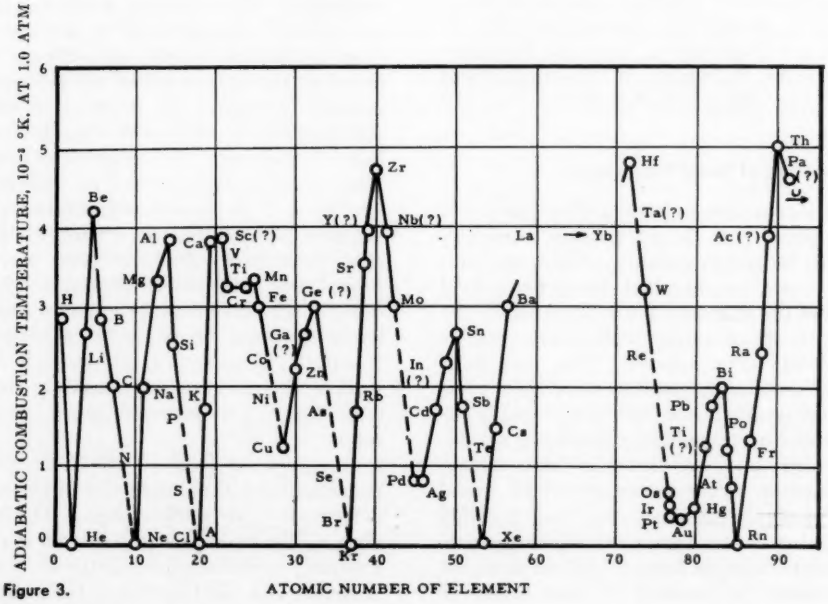


Figure 3.

specific impulse, $I_s$.

$$I_s = \frac{Ft}{m_p g} = \frac{F}{(dm/dt)g} \text{ lbf-sec-lbm}^{-1} \quad (4)$$

The effective exhaust velocity $c$ (impulse per unit mass or thrust per unit mass-rate of flow) is also used. This is equal to $gI_s$.

In applying a propellant to launching a satellite or firing a missile, the important quantity is the burnout velocity of the device. Analysis shows that the burnout velocity, $v_b$, in a vacuum is

$$v_b = g\, I_s \ln \frac{1}{1 - m/M} \quad (5)$$

in which $m$ is the mass of propellant and $M$ is the total mass of the vehicle including propellant.

The relative importance of specific impulse and density of the propellant in designing a rocket depends on the missile propellant weight fraction and certain assumptions made in the design of the missile. Generally, the payload is assumed to be constant. If it is assumed that the propellant tank or chamber is of fixed weight and volume, analysis shows that at a propellant weight fraction of 0.6 an increase in density is 60% as effective in increasing burnout velocity as the same percentage increase in specific impulse. But with the same propellant weight fraction for the missile and the assumption that the propellant weight is fixed, analysis shows that an increase in density is only 10% as effective as the same percentage increase in specific impulse. Thus, if a missile is to be carried by aircraft with limited total weight capacity, improved propellant performance is sought primarily through specific impulse increases; if volume is also limited, density increases are also useful.

Theory shows (*1*, *5*) that the specific impulse is a quantity which depends on the number of moles of gas, $n$, produced per unit weight of propellant, the flame temperature, $T_c$, the heat capacity ratio, $\gamma = c_p/c_v$, and the chamber and exhaust pressures, $P_c$ and $P_e$.

$$I_s = \sqrt{0.434\, nRT_c \left(\frac{2\gamma}{\gamma - 1}\right)\left[1 - \left(\frac{P_e}{P_c}\right)_{(\gamma-1)/\gamma}\right]} \quad (6)$$

A simple shortcut is available for estimating rapidly the specific impulse of certain types of solid propellants from the composition and heats of formation of the ingredients (*6*). However, at this time let us be content with a qualitative understanding of the equation. Equation 6 shows that to increase specific impulse we need to increase the gas volume and the flame temperature. In addition, the heat capacity ratio should be decreased. Little can be done about the heat capacity ratio but the chemist has ways of attacking the other two parameters. Let us take just one, the flame temperature, which is proportional to the exothermicity of the chemical reaction.

The heat of reaction on burning the propellant is a maximum if the oxidizing and reducing agents are present in stoichiometric amount. Larger heats of reaction can be achieved by properly selecting the oxidizing and reducing agents. If we restrict our discussion to the reducing agent and for purposes of example look only at the simplest reducing agents, the metallic elements, we might search for the metal which evolves the most heat when burned with oxygen. Figure 2 shows the molar heats of formation of metal oxides plotted against atomic number (*7*). Another method would be to plot the temperature achieved in burning the metal as shown in Figure 3. Actually, it is most pertinent to plot the heat of formation per gram of oxide because the highest heat evolved per gram is the goal. This last method succeeds in eliminating the heavier elements as promising, as shown in Figure 4.

Detailed calculation of the specific impulse and density of specific compositions may still show the heavy metals to be useful in applications for which their densities compensate for the smaller heat evolution per gram. It is evident from this discussion how improvements can be sought in solid propellants. The extension of this method of attack to non-oxygen containing oxidizers, etc. is straightforward.

The improvement in performance is not limited to improvements produced in the propellant specific

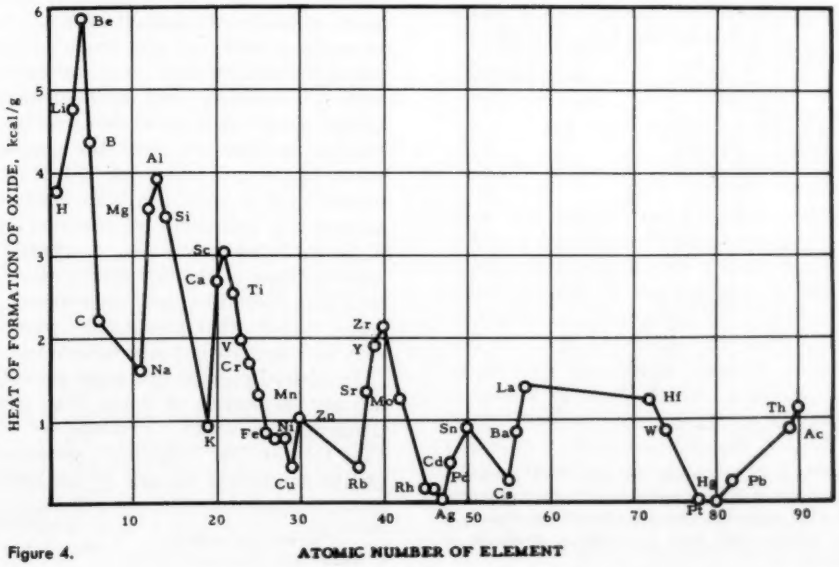


Figure 4.

impulse and density. The chamber weight is a very important factor. The rocket propellant can be incorporated in the motor in several ways: as an end-burning grain, internal-burning grain, or internal-external burning grain. The internal-burning grain permits use of the lightest weight chamber because it protects the walls from exposure to the hot propellant gases. The central perforation of the internal-burning grain is usually of a star shape so that a neutral or flat pressure-time curve will be obtained.

Another important characteristic is the burning rate itself which, ideally, should be of such a magnitude as to permit use of a grain shape in which the length-diameter ratio is of the order of 2 or 3 so that the lightest chamber can be used. Also, the temperature coefficient of chamber pressure (which is related to the pressure exponent and the temperature coefficient of burning rate) should be as small as possible so that the chamber pressure at the highest temperature of operation will not be greatly higher than that at normal temperature.

It is evident from this discussion that the chemist plays an important role in the development of solid-propellant rocket motors. It is his task for each vehicle to discover and develop propellants which have the combination of properties required. Thermodynamics is used in selecting ingredients to deliver the desired specific impulse. Inorganic and organic chemistry are relied on to provide new ingredients of higher energy content. Polymer chemistry is brought into play in processing and in developing the required mechanical properties. Reaction kinetics is involved in modifying the burning rate for every new size of rocket motor. Finally, analytical chemistry provides suitable methods for controlling the processes used. Solid propellant rocketry is an important new occupation for the professional chemist.

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Chem Ed

# LETTERS

*To the Editor:*

I note in your June issue, p. 292, that W. R. Doty of the California Research Corporation has rediscovered the advantages of flexible vacuum connections on filter flasks. I came to the same conclusions over ten years ago (*Chem. & Ind.*, **268**, 1949), and the idea was incorporated into British Standard Specification No. 1739 (1951). However, the fact that it is still impossible to obtain this type of (almost unbreakable) flask commercially except to special order tempts me to think that the idea, like that of the everlasting match, may be too good for it to be a success (commercially).


L. Bretherick

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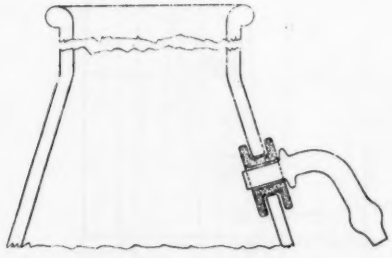
Dagenham, Essex

Editor's Note: Mr. Doty's reply to Mr. Bretherick acknowledges that the "idea of drilling and using a rubber grommet was rediscovered." He adds that Corning Glass Works plans to manufacture these fittings and soon have them available as standard catalogued items.

*To the Editor:*

The excellent article on "Laboratory Safety" by Chamberlain and Jabs, in the September issue of this Journal, raises by implication a question which I should like to see discussed in more detail: "To what extent should a beginning student be warned against non-existent hazards?"

Specifically, I question the example on p. 446, the dilution of concentrated acids. Adding water to concentrated nitric or syrupy phosphoric acid produces a moderate amount of heat, to be sure, but I have never observed any tendency to spattering; the heat produced by dilution of concentrated hydrochloric acid is perceptible but quite negligible; dilution of glacial acetic acid produced no heat detectable by touch. Is it wise to warn the student against adding water to any acid when only one acid presents a serious hazard? It is very nearly an insult to the student to assume that he cannot tell one acid from another—and if he can't, he may come to a bad end anyway—but more serious is the possibility that later on, finding that this precaution was unnecessary, the student will suspect that other precautions were likewise unnecessary and thereby get into serious trouble.

Incidentally, it is my experience that students are already so scared of acids that they underrate the dangers of alkalies. Perhaps we should emphasize that the familiar "slippery" sensation is the result of partial solution of the skin by the alkali.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*Report of the* New England Association of Chemistry Teachers

**Richard L. Gustafson**
Clark University
Worcester 10, Massachusetts

# Polymerization of Metal Chelates in Aqueous Solution

Many metal ions have been shown to form polynuclear hydroxo complexes in aqueous solution. In many cases, including those of $Al^{3+}$ (*1*), $Sc^{3+}$ (*2*), $VO^{2+}$ (*3*), $Cr^{3+}$ (*4, 5, 6, 7*), $Fe^{3+}$ (*8*), $Cu^{2+}$ (*9, 10*), $Sn^{2+}$ (*11*), $Th^{4+}$ (*12*), and $UO_2^{2+}$ (*13, 14, 15*), the initial steps have been demonstrated to lead to the formation of binuclear species according to the reactions.

$$M(H_2O)_x \rightleftharpoons M[OH](H_2O)_{(x-1)} + H^+$$

and

$$2M[OH](H_2O)_{(x-1)} \rightleftharpoons M_2[OH]_2(H_2O)_{(2x-4)} + 2H_2O$$

Here M represents a metal ion, [OH] represents a coordinated hydroxo group, and $x$ indicates the number of coordinated water molecules bound per metal ion. Interaction of the binuclear complexes with additional hydroxyl ions results in many cases in the formation of extremely complex aggregates which usually precipitate in weakly acidic or neutral solution. The degree of formation of large polymers may be reduced in many cases by chelating the metal ions with various polydentate ligands. The tendency of the metal ions to hydrolyze and polymerize is then inhibited because the number of coordination sites available for hydrolysis and olation is reduced and because the positive charge of the metal is lowered.

To date the metal chelates which have been the most extensively studied with respect to their tendency to hydrolyze and polymerize in aqueous solution are those of Cu(II), Fe(III), Zr(IV), and Th(IV) ions. The spacial arrangements of electron pair donor atoms about these metal ions are shown in Figure 1 where it

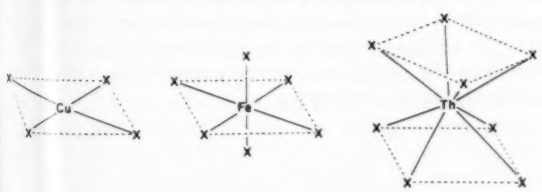



Figure 1. Stereochemical configurations of coordination compounds.

may be seen that the Cu(II) ion may accept four donor groups (indicated by *X*) arranged in a square planar configuration, the Fe(III) ion has six coordinating groups located at the corners of an octahedron, and the Th(IV) and Zr(IV) ions can accept eight donor atoms arranged at the corners of a square Archimedean antiprism. Coordination positions not occupied by donor atoms of the chelating molecules will be filled by water molecules. When the oxygen atom of a water molecule donates an electron pair to the metal ion, the oxygen atom becomes more positive in character, thus increasing the tendency toward dissociation of a positively charged hydrogen ion than is the case for an uncoordinated water molecule. The result is the formation of a hydroxo chelate which may react with another such molecule to form a binuclear diolate chelate or may dissociate an additional hydrogen ion to form a dihydroxo chelate. Typical reactions of Cu(II) chelates formed with bidentate ligands are shown in Figure 2 where the Cu(II)-dipyridyl system is used as an example. The reactions involved and the corresponding equilibrium constants for the hydrolysis and olation of metal chelates may be written as follows:

$$MA(H_2O)_x \rightleftharpoons M[OH]A(H_2O)_{x-1} + H^+ \qquad K_a = \frac{[M[OH]A]\ [H^+]}{[MA]} \tag{1}$$

$$2MA(H_2O)_x \rightleftharpoons (M[OH]A(H_2O)_{x-2})_2 + 2H^+ + 2H_2O \qquad K_D = \frac{[(M[OH]A)_2]\ [H^+]^2}{[MA]^2} \tag{2}$$

$$2M[OH]A(H_2O)_{x-1} \rightleftharpoons (M[OH]A(H_2O)_{x-2})_2 + 2H_2O \qquad K_d = \frac{[(M[OH]A)_2]}{[(M[OH]A)^2]} \tag{3}$$

$$MA(H_2O)_x \rightleftharpoons M[OH]_2A(H_2O)_{x-2} + 2\,H^+ \qquad K_c = \frac{[M[OH]_2A]\ [H^+]^2}{[MA]} \tag{4}$$

Here A represents the ligand molecule and [OH] represents a coordinated hydroxo group.

The technique most commonly employed in the determination of the various hydrolysis and olation constants is potentiometric titration, employing glass and calomel electrodes in conjunction with a *p*H meter. In practice, a solution containing the metal chelate and appropriate supporting electrolyte (employed to minimize changes in activity coefficients) is placed in a thermostatted cell through which nitrogen gas is passed in order to insure a carbon dioxide free atmosphere. Readings of *p*H are taken after the addition of small increments of standard hydroxide solution. The result is a titration curve such as the ones

Presented before the 306th Meeting of the New England Association of Chemistry Teachers at the College of the Holy Cross, Worcester, Mass., May 14, 1960.

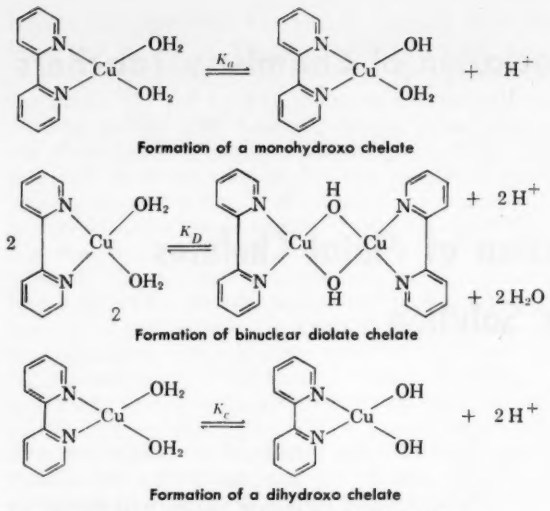



**Figure 2. Hydrolysis and olation of the Cu(II)-dipyridyl chelate.**

shown in Figure 3 for the titrations of Cu(II)-dipyridyl chelates at various concentrations. A steep inflection is observed after the addition of one mole of base per mole of metal chelate, indicating the formation of a monohydroxo chelate and of corresponding polymerization products. Further interaction of the chelate with hydroxide ion is indicated by the buffer region beyond "m" = 1.0.

The following material balance equations may be employed in the region of the titration curve from "m" = 0–1:

$$T_M = [MA] + [M[OH]A] + 2[(M[OH]A)_2] \quad (5)$$

$$T_{OH} + [H^+] - [OH^-] = [M[OH]A] + 2[(M[OH]A)_2] \quad (6)$$

Here $T_M$ is the total analytical concentration of metal ion in all forms, $T_{OH}$ is the total concentration of hydroxide added to the experimental solution, and $[OH^-]$ is the actual hydroxyl ion concentration as

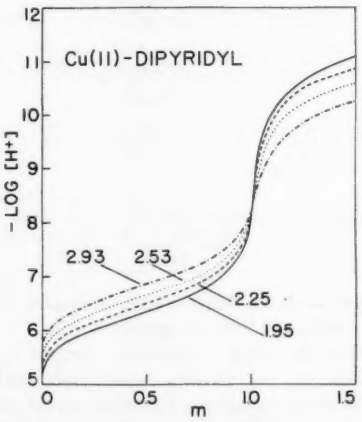



**Figure 3. Potentiometric titration of 1:1 Cu(II)-dipyridyl chelates at 25°. Numbers pertaining to curves refer to negative logarithms of chelate concentrations in moles per liter; m = moles of KOH added per mole of metal chelate; $\mu$ = 0.10 ($KNO_3$).**

calculated from a *p*H measurement. Combination of equations (1), (2), (5), and (6) leads to the slope intercept equation,

$$\frac{[H^+](T_{OH} + [H^+] - [OH^-])}{[MA]} = \frac{2[MA]}{[H^+]} K_D + K_a$$

A plot of $[H^+]$ $(T_{OH} + [H^+]\text{-}[OH^-])/[MA]$ as ordinate versus $2[MA]/[H^+]$ as abscissa using data obtained in the range "m" = 0–1 will give a straight line of slope $K_D$ and intercept $K_a$ if monohydroxo chelates and their corresponding binuclear diolated forms are the only hydrolyzed metal chelate species present in solution. A plot of data obtained for the Cu(II)-dipyridyl system is shown in Figure 4, where a straight line is observed for data obtained over a tenfold range of metal chelate concentration. Many Cu(II) chelates of bidentate ligands have been shown (*16*, *17*) to form binuclear hydroxo chelates. A summary of data obtained for such systems is shown in Table 1.

An interesting observation is that, in general, chelates of the least basic bidentate ligands dimerize to the greatest extent. This is perhaps to be expected

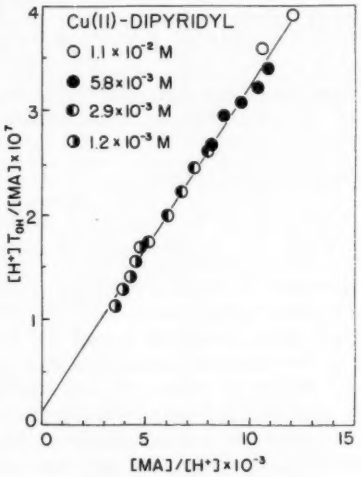
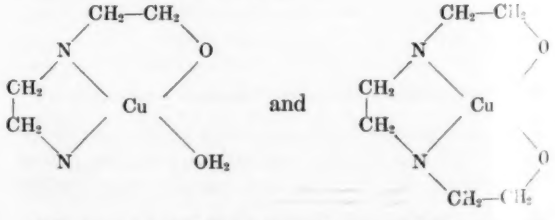


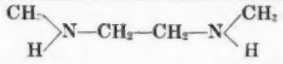
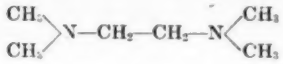
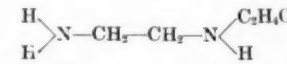
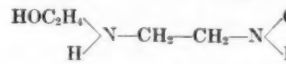
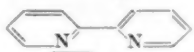
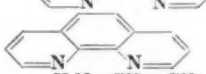
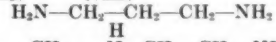
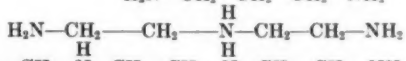
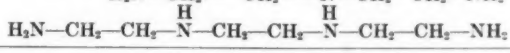

**Figure 4. Plot of data of Figure 3 illustrating presence of binuclear diolated chelate species, $(Cu[OH]A)_2$.**

since a chelate in which the Cu(II) ion forms a weaker bond with a ligand would have a greater affinity for an additional donor group such as a hydroxyl ion. When a third or fourth nitrogen atom is bound to the metal ion, such as in the cases of Cu(II)-diethylenetriamine or Cu(II)-triethylenetetramine, polymerization is not possible although hydroxo species of both chelates are formed. Chelates of N-hydroxyethylethylenediamine and N,N′-dihydroxyethylethylenediamine hydrolyze readily but polymerize only to a small degree, suggesting that the oxygen atoms of the hydroxyethyl groups are bound to the metal ions to form tridentate and tetradentate chelates of the types



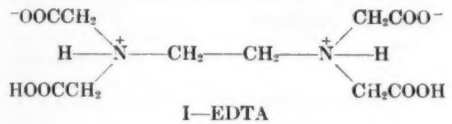

Recent investigations have been carried out concerning the hydrolysis and dimerization of Fe(III),

Table 1. Hydrolysis and Dimerization Constants of Cu(II) Chelates at 25° in 0.1M $KNO_3$

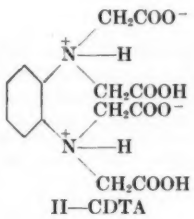
| Ligand | Structural formula | $pK_a$ | log $K$ |
|---|---|---|---|
| N,N′-dimethylethylenediamine |  | 8.09 | 3.8 |
| N,N,N′,N′-tetramethylethylenediamine |  | 8.00 | 3.9 |
| N-hydroxyethylethylenediamine |  | 7.30 | 2.2 |
| N,N′-dihydroxyethylethylenediamine |  | 7.15 | 1.4 |
| α,α′-dipyridyl |  | 7.9 | 5.0 |
| 1,10-phenanthroline |  | 7.8 | 5.0 |
| 1,3-diaminopropane[a] |  | 7.70 | 2.56[d] |
| Diethylenetriamine |  | 9.03 | ... |
| Triethylenetetramine |  | 10.8 | ... |

[a] No supporting electrolyte employed.

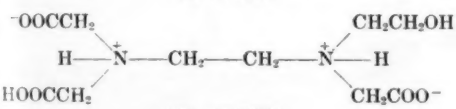
Th(IV), and Zr(IV) chelates of ethylenediaminetetraacetic acid (EDTA—I), trans-1,2-diaminocyclohexanetetraacetic acid (CDTA—II), and N-hydroxyethylethylenediaminetriacetic acid (HEDTA—III).



I—EDTA



II—CDTA



III—HEDTA

In Table 2 are listed values of $pK_a$ and log $K_d$ obtained for various EDTA chelates. Although the basicity of these chelates, as indicated by the $pK_a$ values, increases in the order Zr < Th < Fe, the dimerization constants increase in the order Fe < Zr < Th. The lower tendency toward dimer formation of the Zr(IV) chelate relative to that of the chelate of the larger Th(IV) ion may be due to steric hindrance caused by the small size of the central zirconium atom. The fact that the Fe(III)-EDTA chelate dimerizes at all is perhaps at first surprising. A priori one might assume that polymerization is unlikely since the metal ion is completely coordinated by six donor groups. However, there is a decided tendency for one of the weakly basic acetate groups of the Fe(III)-EDTA chelate to be displaced by a hydroxo group. Displacement of a second acetate group permits dimerization to occur. The energy required for displacement of these acetate groups is sufficient that the tendency toward polymerization is less than that observed for EDTA chelates of Zr(IV) and Th(IV) ions which have coordination numbers of eight and which can undergo dimerization without displacement of acetate donors.

Results obtained for hydrolysis and dimerization of Fe(III) and Th(IV) chelates of CDTA are compared with those of EDTA chelates in Table 3. Here it will be noticed that although the tendency to hydrolyze of Th(IV)-CDTA is less than that for Th(IV)-EDTA, the equilibrium constants, $K_d$, for the formation of the binuclear chelates are identical within experimental error. It has been suggested by Bogucki and Martell (*20*) that the equivalence of the two dimerization constants is the result of two opposing tendencies: (1), the greater tendency for dimerization of the Th(IV)-CDTA chelate as a result of stronger binding strength

Table 2. Hydrolysis and Olation of EDTA Chelates at 25°

| Metal | $pK_a$ | log $K_d$ |
|---|---|---|
| Fe(III)[a] (*18*) | 7.58 | 2.95 |
| Zr(IV)[b] (*19*) | 6.2 | 3.5 |
| Th(IV)[c] (*20*) | 7.04 | 4.3 |

[a] In 1.0 *M* KCl.
[b] In 0.1 *M* KCl.
[c] In 0.1 *M* $KNO_3$.

of the OH group and (2), the somewhat greater steric effects for the CDTA chelate which might inhibit dimer formation. The comparison of hydrolytic tendencies of Fe(III)-CDTA and -EDTA chelates shows the expected trend, where the more stable CDTA chelate hydrolyzes and dimerizes to a lesser extent than does the less stable Fe(III)-EDTA chelate.

Table 3. Hydrolysis and Olation of EDTA and CDTA Chelates at 25°

| System | $pK_a$ | log $K_d$ |
|---|---|---|
| Th(IV)-EDTA[a] (*20*) | 7.04 | 4.3 |
| Th(IV)-CDTA[a] (*20*) | 7.85 | 4.3 |
| Fe(III)-EDTA[b] (*18*) | 7.58 | 2.95 |
| Fe(III)-CDTA[b] (*18*) | 9.32 | 1.01 |

[a] In 0.1 *M* $KNO_3$.
[b] In 1.0 *M* KCl.

Hydrolysis reactions of HEDTA chelates are more complex than is the case for systems previously mentioned, although the initial reactions are still those of formation of a simple monohydroxo chelate and its corresponding dimerization product. Titration of the Th(IV)-HEDTA chelate results in the reaction of $1^2/_3$ moles of hydroxide ion per mole of metal chelate in producing a unique hydrolysis product. Plots of data obtained in the region "m" = 0–0.4 yield straight lines similar to those of Figure 4, showing that the initial reactions are those indicated by equations (1–3). Titration of the Fe(III)-HEDTA chelate gives an expected inflection at "m" = 1.0. A summary of data obtained for Fe(III)- and Th(IV)-HEDTA chelates is shown in Table 4. Here it may be seen that the tendency to dimerize is much greater for Th(IV)-HEDTA than for the Fe(III) chelate. In addition the value of $K_d$ is somewhat less for Fe(III)-HEDTA than for Fe(III)-EDTA. The low values for $pK_a$ for both HEDTA systems suggest that the first hydrolysis step does not involve formation of a hydroxo chelate but that a proton is dissociated from the coordinated oxygen atom of the hydroxyethyl group.

**Table 4. Hydrolysis and Olation of HEDTA Chelates at 25°**

| Metal | $pK_a$ | log $K_d$ |
|---|---|---|
| Fe(III)[a] (*18*) | 4.1 | 2.4 |
| Th(IV)[b] (*21*) | 5.4 | 5.2 |

[a] In 1.0 *M* KCl.
[b] In 0.1 *M* $KNO_3$.

Although it has been shown that many metal chelate systems hydrolyze to form simple binuclear diolated chelates, many systems do not follow this pattern. Representative of systems which undergo more complex reactions are $UO_2$-pyrocatechol-3,5-disulfonate (trimeric at *p*H 5.3) (*15*), 2:3 Th(IV)-pyrocatechol-3,5-disulfonate (binuclear but unhydrolyzed at *p*H 5) (*22*, *23*), and Th(IV)-HEDTA (hexameric at *p*H 7) (*24*). The determination of equilibrium constants for the reactions involved requires individual treatment for each system. Determination of the degree of aggregation has been effected in several cases by the use of solvent extraction and ultracentrifugation techniques. The determination of molecular weights of polynuclear chelates from data obtained upon sedimentation in a strong gravitational field will surely find much use in future studies in this field.

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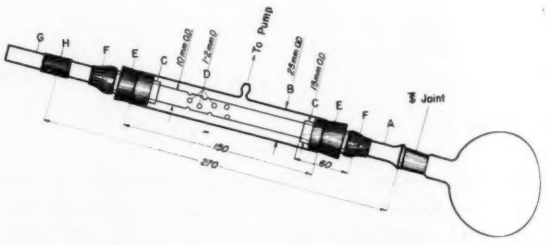
(24) Gustafson, R. L., and Martell, A. E., unpublished results.


## A Convenient Device for the Evaporation of Solvents


**Yair Sprinzak**

Weizmann Institute of Science, Rehovoth, Israel


The simple device shown in the figure has been used advantageously in this laboratory for the rotatory evaporation of solvents. It can be used in conjunction with an ordinary laboratory motor, suspended on a stand.




The outer fixed tube *B* accommodates the rotating tube *A* by means of pairs of rubber stoppers *E*, glass tubings *C*, and rubber sleeves *F*. Tube *A* is perforated along its middle section and terminated by a ground joint; its upper end is connected to the drive *G* of a motor by a rubber sleeve *H*. The flask is immersed in a small water bath suspended on a stand. Sleeves *F* are lubricated with glycerine. For the lower sleeve *F*, it is advisable to introduce, before use, a few drops of lubricant between tube *A* and glass tubing *C*; this can be done by wetting tube *A* by means of a thin pipet inserted through the pump outlet.

Chem Ed

# BOOK REVIEWS

### Elements of Physical Chemistry

*Samuel Glasstone*, Consultant to the U. S. Atomic Energy Commission, and *David Lewis*, The City College of New York. 2nd ed. D. Van Nostrand Co., Inc., Princeton, New Jersey, 1960. v + 758 pp. Figs. and tables. 16 × 23.5 cm. $8.50.

This second edition of Glasstone's "Elements" is a considerably more extensive revision than many. In addition to quite a few minor rewritings of sections and rearrangements and expansions of material, two major changes have been made: the discussion of the properties of gases and of thermodynamics has been moved up to the beginning of the book; and a considerable amount of new material has been added.

The shift of thermodynamics has allowed a thermodynamic derivation of the Clapeyron equation before it is needed for the discussion of vapor pressure equilibria, but otherwise appears to have only esthetic value. It has the disadvantage that the discussion of the statistical significance of entropy, etc., must be deferred until a later chapter, after the discussion of quantization of energy in connection with atomic and molecular structure. This reviewer preferred the arrangement in the first edition, although the content is much improved.

New material is scattered throughout the book, but the main new topics, all of which markedly improve the book, are the statistical significance and calculation of entropy, molecular spectra, primary processes and other topics in photochemistry, and nuclear chemistry.

As in the first edition, the format is attractive and convenient, the exposition is clear and easy to follow, and answers are given to all problems.

In summary, this reviewer feels that the book is on a par as a text with the best of the "standard" physical chemistry texts.

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### The Science Study Series. Volumes 7–10

Doubleday & Co., Inc., Garden City, New York, 1959. Available to secondary school students and teachers through Wesleyan University Press, Inc., Columbus, Ohio. Figs. and tables. Each volume, 11 × 18 cm. Paperbound. Volume 7, 320 pp., $1.45. Volume 8, 160 pp.; Volume 9, 235 pp.; Volume 10, 200 pp. Volumes 8–10 each $0.95.

Four more volumes in this welcome series are now available. [See THIS JOURNAL, 37, 54 (1960)]. Volume 7, "Crystals and Crystal Growing," by Alan Holden and Phylis Singer, can be described in one word, "magnificent!" There is no better book for the Science Fair enthusiast. Not only are projects suggested and directions provided, but most importantly, the beginner will find the book so fascinating that he will learn some solid state physics before he can stop himself. Clear drawings, imaginative diagrams, and beautiful color photographs supplement a carefully organised and lucidly written account of "Order in Nature."

"The Physics of Television—Vision Beyond Sight," Volume 8, by Donald G. Fink and David M. Lutyens, and "Waves and the Ear—What We Hear and How," Volume 9, by Willem A. Van Bergeijk, John R. Pierce, and Edward E. David, Jr., follow the familiar pattern of the rest of the series. They tell the beginner much, but also make the important emphasis on how much there is yet to learn.

Professor I. Bernard Cohen of Harvard has added an interesting historical dimension to the series with his "The Birth of a New Physics," Volume 10. Fortunately the subtitle, "From Copernicus to Newton" clarifies the term *new*. Physics is mechanics. Any time students are led to ask the questions posed by the intellectual giants of the past in the proper context, their appreciation of how to solve problems in the present day is heightened.

Every college science professor should find the time to read these. If he doesn't, he may be in an embarrassing spot when his classes begin to consist of students who have!

W. F. K.

### Inorganic Chemistry

*Jacob Kleinberg, William J. Argersinger, Jr.*, and *Ernest Griswold*, all of the University of Kansas, Lawrence. D. C. Heath & Co., Boston, 1960. viii + 680 pp. Figs. and tables. 17.5 × 24 cm. $10.75.

Almost any textbook designed for use in courses in inorganic chemistry at the senior and/or first year graduate level is likely to attract immediate attention and be received with excessive enthusiasm. Certainly such was the case upon publication of the well-known and widely-used text by Professor Therald Moeller in 1952. But any authors who attempt to fill this particular need face a grim task. For many years there was not a single textbook widely adjudged to be acceptable and courses in inorganic chemistry the country over consequently were subject to wide variations in content that reflected the interests, training, and inclinations of the individual teacher.

In the opinion of this reviewer, the volume by Kleinberg, Argersinger, and Griswold represents the best compromise thus far. The book is well written and there is a consistency of style that is unusual in cases of multiple authorship. The book is well-balanced with respect to choice of subject-matter content; and this is the most difficult task of all. There can be no hesitation whatever in predicting that this book will quickly become the single most widely used text of its kind.

Each teacher who uses this or any other similar textbook will, however, have his own characteristic reservations with respect to what is omitted as well as what is included. The following reactions and criticisms therefore should not be construed as derogatory; rather they should be looked upon as inevitable.

### Reviewed in This Issue

*Samuel Glasstone* and *David Lewis*, Elements of Physical Chemistry.

The Science Study Series. Volumes 7-10

*Jacob Kleinberg, William J. Argersinger, Jr.*, and *Ernest Griswold*, Inorganic Chemistry

*Robert Kunin*, Elements of Ion Exchange

*D. H. Everett*, An Introduction to the Study of Chemical Thermodynamics

*G. E. Francis, W. Mulligan*, and *A. Wormall*, Isotopic Tracers

*F. Smith* and *R. Montgomery*, Chemistry of Plant Gums and Mucilages and Some Related Polysaccharides

*Galen W. Ewing*, Instrumental Methods of Chemical Analysis

Edited by *Dael Wolfe*, Symposium on Basic Research

*George C. Pimentel* and *Aubrey L. McClellan*, The Hydrogen Bond

*C. W. Carter, R. V. Coxon, D. S. Parsons*, and *R. H. S. Thompson*, Biochemistry in Relation to Medicine

*Jay A. Young*, Elements of General Chemistry

*Phillip Pollack*, Careers and Opportunities in Chemistry

This book is subdivided into three major sections. Part I (207 pages) entitled Atomic Structure and Properties consists of a quite abbreviated account of background information. The content of Chapter 1 is purely historical and could well have been omitted in its entirety. Chapter 2 entitled Quantum Mechanics and Atomic Structure is an unduly abbreviated version of so broad a topic and most teachers will probably find that considerable elaboration is necessary. It is unfortunate that the space essentially wasted in Chapter 1 was not allocated to such an elaboration. The remainder of Part I is devoted to the usual physical principles that are important to the study of properties of the elements in relation to the periodic classification. Although bond types are discussed in this section, ligand field theory is deferred to a later chapter (in Part II) where this topic is disposed of summarily in two pages. Few teachers are likely to feel that this important topic has been given the emphasis that it merits.

Part II (84 pages) consists of only two chapters; one is devoted to Coordination Compounds, the other to Reactions in Nonaqueous Systems. In view of the limited time available in most courses, the treatment of these topics seems entirely adequate and represents coverage as comprehensive as one could hope to achieve.

Part III (374 pages) consists of a systematic study of the periodic table, by groups of elements; physical properties are emphasized throughout this section and purely descriptive material is kept to a minimum. It is in the writing of this part of the book that the authors repeatedly faced the difficult problem of deciding what to include and what to omit. Here, the present authors have succeeded where others have failed, i.e., they have avoided the temptation to bog down in a morass of detail relating to specific topics. As a result, however, teachers who use this book will perhaps be annoyed to note the omission of a favored topic or to feel that proper emphasis has not been given. As an example, the discussion of the boron hydrides is typical. It is unfortunate that the topological approach of Lipscomb is not included; even less understandable is the absence of any reference to the Longuet-Higgins interpretation of the structure of diborance.

The authors have achieved a fine balance between emphasis upon the nontransitional and transitional elements. The last two chapters in Part III are particularly welcome in that they are concerned with a brief account of the chemical and physical properties of the elements of the lanthanide and actinide series.

Finally, this reviewer's over-all impression of this book can be summed up by the opinion that, of the books now available, this one does not have a serious competitor.

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## Elements of Ion Exchange

*Robert Kunin*, Rohm and Haas Company, Philadelphia. Reinhold Publishing Corp., New York, 1960. ix + 164 pp. Figs. and tables. 13 × 19 cm. $5.75.

The author states in the Preface that "there is a definite need for a book devoted to this topic (ion exchange) that is not written for the expert or specialist, but for the uninitiated who have only a slight background of basic chemistry." This little book is the author's valiant effort in the difficult task of meeting this need.

The uninitiated is sure to be puzzled at times, for example, when he encounters chemical formulas occupying almost one-half page or when he reads on p. 42: "Specific uses of the polymer may make some or all of the following properties important: (1) pressure drop, (2) hydraulic expansion, (3) volume change between ionic forms, (4) solubility or content of extractable material, (5) color throw." It is to be hoped that he will read on even though he fails to comprehend completely some parts because he will find much valuable and interesting information about the manufacture of ion-exchange resins, their properties, and their applications. The last point receives the greatest emphasis.

More careful editing would have eliminated inconsistencies in writing the formulas of ions, such as $UO_2(SO_4)_3^{=\,=}$ and $UO_2(SO_4)_3^{+4\,-}$; methods of designating valence number, such as Cr(VI) and $U^{VI}$; in the use of symbols, where Co and $C_o$ are used interchangeably; and in the hyphenation of compound adjectives, such as ion-exchange materials and cation exchange capacity.

The treatment of catalysis on pp. 128 and 129 under Chapter 8, Miscellaneous Applications, is largely a repetition of the section on catalysis on pp. 82 and 83 under Principles of Ion-Exchange Applications. Similarly, much of the material on pp. 74 to 81 on Removal of Ions, Concentration of Ions, and Fractionation of Mixtures, is repeated on pp. 117 to 122 under Analytical Chemistry.

In spite of these shortcomings, the book fulfills well its purpose of providing a general introduction to ion exchange.

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## An Introduction to the Study of Chemical Thermodynamics

*D. H. Everett*, The University of Bristol. Longmans, Green & Co., Inc., New York, 1959. xx + 240 pp. Figs. 15 × 22 cm. $5.75.

The author of this book believes that the difficulties of thermodynamics can be circumvented by teaching the subject backward. Accordingly, in a book of 12 chapters he does not present the laws of thermodynamics until the eleventh chapter.

This reviewer believes that the author is so obsessed with the difficulties of thermodynamics that he makes the subject more difficult than it needs to be. Two examples of this statement are provided by the author's preference for using affinities instead of free energies and by his excessive use of mechanical analogies to illustrate the application of thermodynamic equations.

Affinities are an entirely superfluous complication of the subject, as are most of the mechanical analogies. A student using this book would have to spend so much time trying to understand and *remember* (p. 62) the irrelevant mechanical analogies that he would have much less time to learn the applications of thermodynamics to chemistry.

This book provides an excellent illustration of the present reviewer's contention, in "The Semantics of Thermodynamics," THIS JOURNAL, 23, 54 (1946), that one of the principal difficulties in the study of thermodynamics is the poor semantics of some of its teachers and textbook writers. For example, the author not only uses the confusing and long-discredited term *heat content* for $H$; he actually seems to believe what the term implies: that a system has heat in it (p. 19). On the contrary, the only place for heat in all of thermodynamics is in the equation $\Delta E = q - w$ (and in the related equations) in which heat can mean only energy *being transferred* because of a temperature difference. No system has heat *in* it. The sun has *no* heat *in* it; it has plenty of $TS$ energy but *no q in it.*

Another closely related example of semantic confusion in this book is the author's use of $\Delta Q$ and $\Delta W$ to stand for $q$ and $w$ in the preceding equation, thus implying that heat and work are properties of a system (like $F$, $E$, or $H$). Again, as with $H$, the author's confusing terminology tricks him into making statements which seem to indicate that he actually believes work can be stored up in a system (p. 9) and that heat also can be stored in a system (p. 163).

Probably this use of $\Delta Q$ and $\Delta W$ alone would prevent adoption of the book by most teachers. However, one chapter is an exception to the general confusion. The chapter on electrochemical systems is the best brief discussion this reviewer has ever seen. It avoids calling the same electrode a *cathode* while a cell is being charged and an *anode* while the cell is discharging, by reserving the terms for use only when the cell is being charged and employing the terms *positive* and *negative electrodes* when the cell is discharging. The sign conventions are clearly stated and easily followed. Standard electrode potentials are listed (according to the IUPAC recommendation) as reduction potentials, thus permitting the fluorine electrode to be placed at the top of the table with a positive voltage and the lithium electrode to be at the bottom with a negative voltage.

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